New Coordination Polymers of Copper(I) and Silver(I) with Pyrazine and Piperazine: A Step Toward “Green” Chemistry and Optoelectronic Applications

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Abstract. Five coordination polymers and one hexanuclear cluster have been obtained and their crystal structure determined upon reaction of Cu(I) or Ag(I) precursors with pyrazine (Pyz) or piperazine (Ppz). Five complexes are mixed-imine-ligand with anionic-fluorinated pyrazolate $[3,5\text{-}(CF_3)_2Pz]^-$ ($[Pz^F]^-$) besides Pyz or Ppz, whereas the sixth had the neutral diimine as a single chromophore. Complexes **1**-**3** are isomers of the same Cu/Pz^F/Pyz composition with the same or different unit cell stoichiometry, namely $\{Cu_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_3(CH_2Cl_2)\}_\infty$ (**1**•CH_2Cl_2), $\{Cu_2[3,5\text{-}(CF_3)_2Pz]\}_2(Pyz)_2\text{•toluene}\}_\infty$ (**2**•toluene), and $\{Cu_3[3,5\text{-}(CF_3)_2Pz]_3(Pyz)_{1.5}\text{•1.5benzene}\}_\infty$ (**3**•1.5benzene), respectively. Altering only the metal attains $\{Ag_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_2\text{•2benzene}\}$ (**4**•2benzene) while also changing the neutral diimine attains $\{Ag_2[3,5\text{-}(CF_3)_2Pz]_2(Ppz)\}_\infty$ (**5**). Using Pyz without an anionic imine yields $\{[Cu(Pyz)(MeCN)_2][BF_4]\}_\infty$ (**6**). The crystal structure of **1** shows two trimers linked together with two pyrazine ligands. Crystals of **2** represent a metal-organic framework (MOF-TW1) with significant surface area (1278 m^2/g) and porosity (23.7% void volume) without considering toluene adsorbates in channels. MOF-TW1 was obtained serendipitously upon a reaction attempt to attain a mixed-metal product, instead attaining a Cu(I)-only product with interconnected 4-coordinate dinuclear units. Likewise, **3** was obtained through a transmetalation of all Ag atoms in **4** to replaced them by Cu atoms. Three reactions (to obtain **1**, **4**, and **5**) were successfully carried out by both solvent-mediated and solventless transformations, whereas **2** and **3** were obtained only by solvent-mediated reactions while **6** was attainable only by solventless transformations. The solventless transformations occurred either by sublimation and vapor diffusion or by mechanical grinding *at ambient laboratory conditions* – without the aid of heating, high pressure, vacuum, or any automated equipment. All transformations could be monitored by the human eye as the reaction progresses, as evidenced by progressive discoloration and/or luminescence changes. All crystal structures were obtained with the aid of conventional crystal growth methods from organic solvents for bulk products obtained from both solvelntless and solvent-mediated reactions. Powder X-ray diffraction was used to compare bulk products with one another and the crystallographic products. All Cu(I) products are colored and non-luminescent; the progress of their vapor diffusion-based solventless reactions can be followed by gradual discoloration of white solid reactants and/or quenching precursor's phosphorescence. Both Ag(I) products were colorless with **4** being luminescent but not **5**.

Introduction

There has been great interest in the design of coordination polymers with unique structural architecture, topology, and/or morphology. Such compounds are of interest for supramolecular chemistry and crystal engineering of porous metal-organic frameworks (MOFs) or other functional coordination polymers -- as potential materials with enabling properties for a variety of applications (e.g., gas storage and separation, heterogeneous catalysis, magnetism, electrical conductivity, photo-/electro-luminescence for inorganic/organic LEDs, etc.).[1]

Significant efforts have been made to investigate factors that strongly impact the self-assembly of supramolecular architectures of coordination polymers (CPs) -- such as the coordination geometry of metal/metal cluster centers,[2] structure of the organic ligands and/or their substituents,[3] identity of counterions in ionic CPs,[4] pH alteration where relevant,[5] reaction temperature, [6] M:L stoichiometry,[7] solvent properties,[8] presence or absence of a template effect,[9] -- and synthetic method variation (e.g., typical Schlenk or vacuum line techniques, hydrothermal or solvothermal methods, microwave-assisted syntheses, and various solvent-free transformations).[10] The latter topic has been reviewed by Petrukhina[11] and by Balaz et al.,[12] offering complementary insights upon solvent-free preparation of coordination polymers and metal-organic frameworks that have attracted significant attention recently,[13] as such transformations represent a step toward "green chemistry" by addressing significant environmental and public health concerns.[14] A number of solvent-free reactions occur more efficiently, selectively, and easily than reactions carried out in solvents. Solvent-free reactions obviously are preferred and imperative in industrial fields because they provide less-hazardous and lower-cost chemical procedures. In many cases, the products obtained from solvent-free reactions are completely different from those in solution phase reactions, due to the effects of solvent-mediated vs solvent-free environment on the spatial orientation or packing in the crystalline materials, hence providing variable degrees of stereoselectivity or other isomeric and reactivity pathways.[13a-b] Grinding the metal precursor and organic ligand has been one of the most effective mechanochemical approaches to prepare discrete metal complexes.[13b-g]

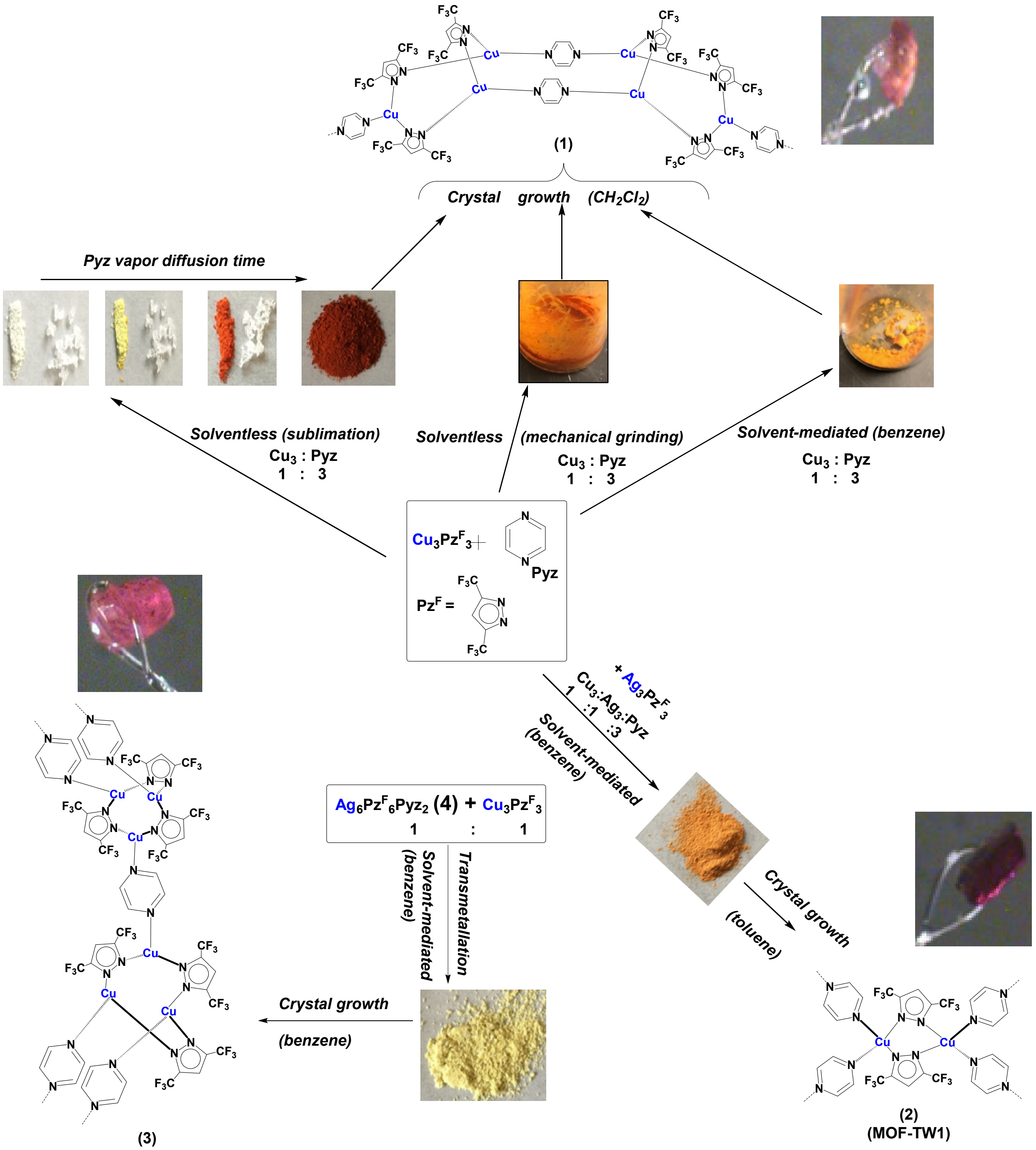
In this paper, we report the synthesis of a new class of d^{10} coinage metal complexes upon reaction of Cu(I) and Ag(I) azolate cyclotrimers (known for remarkable photophysical and bonding properties)[15] or metal salts with *N*-donor organic solids to attain mixed-ligand or single-ligand CPs, respectively. We obtained six products that have been analyzed by single crystal X-ray diffraction. Among the crystallographic products, five complexes are mixed-imine-ligand with anionic-fluorinated pyrazolate $[3,5\text{-}(CF_3)_2Pz]^-$ besides Pyz or Ppz, whereas the sixth had the neutral diimine as a single chromophore. The molecular/supramolecular structural and optical properties (including multi-chromic behavior)[16,15f] are investigated as a function of chemical variables (same vs different metal or metal precursor, transmetallation, saturated vs conjugated ligand, and mixed-ligand vs single-ligand variations), stoichiometry, reaction conditions (mechanochemical vs sublimation and both vs solvent-mediated transformations), and whether the structure or composition is retained or altered upon subjecting the crude product of a given transformation to further crystal growth.

Previous research showed that bridging diimine ligands can affect the structural and electronic properties of the resulting compounds.[17] This work focuses on reactions of monovalent silver and copper complexes with aromatic and aliphatic cyclic *N*-donor bridging ligands. One of the synthetic routes herein include a convenient, economical, and potentially "green" method of synthesis for d^{10} coinage metals complexes with a bridging *N*-donor conjugated diimine (i.e., pyrazine = Pyz) or saturated diamine (i.e., piperazine = Ppz) to ligate the metal cyclotrimer or salt precursor. Given the well-known adverse environmental and health impacts of organic solvents, synthetic methods with reduced dependence on organic solvents are worthwhile. To this effect, the possibility of investigating the reactions herein by solvent-free methods has been discovered as a result of observations during undergraduate research and teaching-discovery laboratories. The corresponding author, who was the instructor of these laboratories, noticed that when the undergraduate students left the starting solid materials next to each other, discoloration was taking place in multiple instances. Further detailed investigations then led us to systematically carry out various solventless transformations, both those described herein and others,[18] to evaluate their effectiveness versus solvent-mediated reactions, as this has become a new research direction in this group.

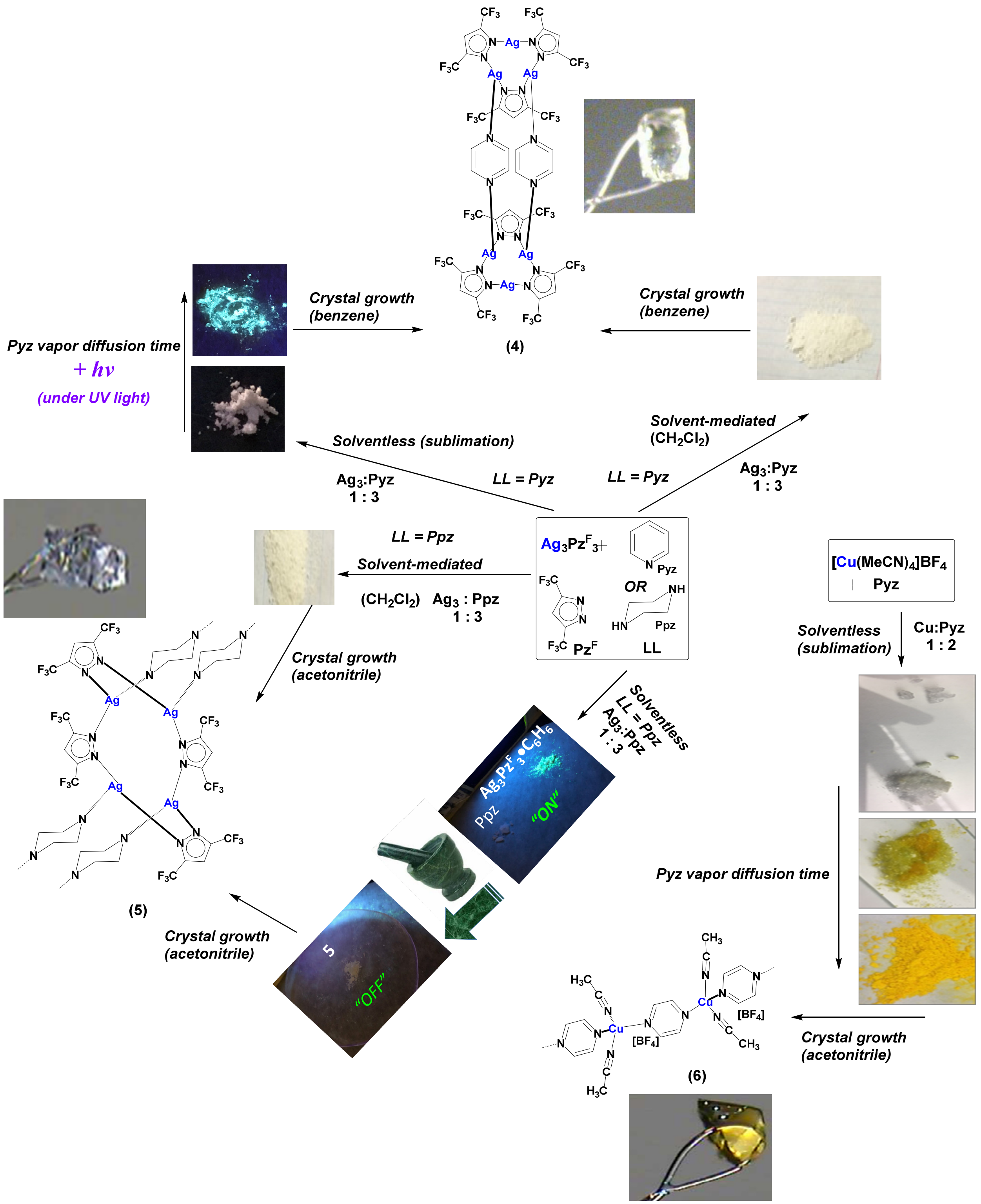
Results and Discussion

Synthesis and Reactivity: Schemes 1-2 summarize the reactions and structures of the various products obtained in this work. The cyclic trinuclear copper(I) and silver(I) pyrazolates $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ are synthesized according to an established literature procedure,[19] and likewise for the free Cu(I) precursor tetrakis(acetonitrile)copper(I) tetrafluoroborate, $[Cu(MeCN)_4]BF_4$.[20] The products are obtained upon reacting a small molar excess of 1,4-pyrazine (Pyz) or 1,4-piperazine (Ppz) with the aforementioned precursors (with respect to a 1:3 mixing stoichiometry for $M_3Pz^F{}_3$ or 1:2 for $[Cu(MeCN)_4]BF_4$ reactions) in benzene/toluene/dichloromethane for the solvent-mediated transformations. Solventless transformations with the same mixing stoichiometries entailed mechanical grinding as well as simply exposing the solid metal precursor to the ambient vapor pressure of the Pyz volatile solid (whereas Ppz is not volatile so its solventless reactions are investigated only via mechanical grinding). The ultimate crystallization products, following crystal growth from dichloromethane, benzene, toluene, or acetonitrile by slow evaporation were $\{Cu_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_3\bullet CH_2Cl_2\}_\infty$ (**1**$\bullet CH_2Cl_2$), $\{Cu_2[3,5\text{-}(CF_3)_2Pz]\}_2(Pyz)_2\bullet$toluene$\}_\infty$ (**2**•toluene), $\{Cu_3[3,5\text{-}(CF_3)_2Pz]_3(Pyz)_{1.5}\bullet$1.5benzene$\}_\infty$ (**3**•1.5benzene), $\{Ag_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_2\bullet$2benzene$\}$ (**4**•2benzene), $\{Ag_2[3,5\text{-}(CF_3)_2Pz]_2(Ppz)\}_\infty$ (**5**), and $\{[Cu(Pyz)(MeCN)_2][BF_4]\}_\infty$ (**6**). Thus, the final stoichiometry obtained in the single crystal products did not always follow the same mixing stoichiometry (i.e., it was the same only for **2**). Indeed, even when reaction conditions to obtain **5**, for example, were varied to examine variations of the mixing stoichiometry of Ppz:Ag_3 to include 2:1, 3:1, and 6:1, the same crystallographic product was nevertheless obtained. Silver complexes are air-stable in both the solid-state and solution; they are soluble in organic solvents such as dichloromethane, acetonitrile, acetone and tetrahydrofuran, whereas the copper complexes are rather air-sensitive in those solutions but air-stable in the solid state. The three reactions to obtain the bulk solid powders of **1**, **4**, and **5** were successfully carried out by both solvent-mediated and solventless transformations before crystal growth. Meanwhile, the synthesis of **2** and **3** proceeded only by solvent-mediated reactions while **6** was attainable only by a solventless process – all likewise followed by crystal growth of the crude product. In addition to the solvent-mediated pathway, solventless reactions involving pyrazine can be carried out by vapor diffusion upon spontaneous sublimation at room temperature (without heating solid pyrazine) onto the metal precursor, whereas all metal precursor/ligand combinations are susceptible to reactions by mechanical grinding. The reaction progress in all six products could be monitored by a color change (in the physical and/or luminescence color). Whereas all Cu(I) complexes (**1-3** and **6**) exhibit permanent discoloration, the Ag(I)/Pyz product **4** is luminescent while the formation of the Ag(I)/Ppz analogue **5** can be followed by quenching of the luminescence of the benzene solvate[21] of the $Ag_3Pz^F{}_3$ trimer precursor upon mechanical grinding (Schemes 1-2). The metal precursor of **6**, $[Cu(MeCN)_4]BF_4$, is a non-luminescent white solid that exhibits discoloration upon reaction with pyrazine. On the other hand, the progress of $Cu_3Pz^F{}_3$-based transformations could be monitored by both absorption and emission color changes; i.e., via permanent discoloration of the white $Cu_3Pz^F{}_3$ solid and the complete quenching of its bright orange phosphorescence[15a,b,f] upon introduction of pyrazine. Single crystals of all six samples were obtained by crystal growth from organic then their structures were determined by X-ray crystallographic analysis. In **1**–**5**, the Ag(I) or Cu(I) atoms are connected to the pyrazolate, which act as a chelating ligand. As in other compounds that contain fluorinated pyrazolates,[19,22] the complexes herein also exhibit a good degree of solubility in most common organic solvents. The rigidity and aromaticity of the ligands including pyrazine and piperazine can also affect the coordination mode of the metal atom. For example, the different structure of **4** vs **5** (triclinic vs monoclinic) is possibly due to the different *N*-donor ligand in the two reactions. Schemes 1-2 summarize the variation of the product structure and color upon varying the synthetic transformation to ultimately attain the aforementioned crystallographic products **1-6**.

Three products (**1**-**3**) that represent polymorphs or constitutional isomers of the same CuPz^{F}Pyz combination but whose structure varies based on the synthetic route. While **1** and **3** are crystallographic polymorphs with a very similar molecular structure comprising 3-coordinate Cu(I) centers, **2** is a distinct composition of matter comprising interconnected 4-coordinate Cu(I) tetrahedral repeat units. The Pyz:Cu:Pz^F mixing stoichiometry of 1:1:1 was preserved for the crystallized product **2**, whereby each Cu(I) center was coordinated by two Pyz and two Pz^F bidentate ligands bridging it to the adjacent Cu(I) center. On the other hand, crystals of both **1** and **3** had a 0.5:1:1 respective ratio such that only one Pyz bridges adjacent Cu(I) trigonal-planar centers with the two other coordination positions occupied by Pz^F. Adding further excess of Pyz during the synthesis of **1** attained the same single crystals. For **1**, both the *solventless* and solvent-mediated transformations when the intended starting materials were used (i.e., $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and Pyz in 1:3 stoichiometry) followed by crystal growth in benzene/dichloromethane attained this product as dichloromethane solvate, $\{(\mathbf{1}\bullet CH_2Cl_2)\}_\infty$. Indeed, this same light maroon crystallographic product was obtained from solventless and solvent-mediated bulk products that exhibit different colors (Scheme 1) and different PXRD patterns (vide infra) from one another and from the ultimate crystallographic product. Our attempt to obtain a mixed-metal product by mixing $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ in another *solvent-mediated* reaction has attained, instead, a purely copper complex as toluene solvate, $\{(\mathbf{2}\bullet\text{toluene})\}_\infty$, that did not include silver and was a constitutional isomer of complex **1** with a greater pyrazine content. The role of silver in the formation of **2** among other polymorphs/constitutional isomers of the same CuPz^{F}Pyz composition is not yet understood; we are in the process of investigating the effects of further alterations of reaction routes upon the exact composition and/or structure of various products. Crystallographic analysis has revealed that **2** is, indeed, a metal-organic framework we dub “MOF-TW1” (vide infra). Finally, complex {(**3**•1.5benzene)}$_{\infty}$, was yet another form of the same CuPz^{F}Pyz composition; specifically, it is polymorph of **1** and a constitutional isomer of **2** (i.e., with the same pyrazine content as in **1** but lower than in **2**) that was obtained upon *transmetallation* of its AgPz^{F}Pyz congener, (**4**•2benzene), in a solvent-mediated transformation from benzene this time. These observations suggest that both the reaction route (starting materials, solventless vs solvent-mediated, or reaction solvent for the latter) and the crystallization method play a significant role in identifying the ultimate crystallographic product of the mixed-ligand copper coordination polymers species **1**-**3** of the same CuPz^{F}Pyz chemical composition. The versatile colors and PXRD (vide infra) patterns of the solventless and solvent-mediated crude products obtained suggest the presence of additional polymorphs or constitutional isomers besides the six products identified by single crystal XRD analysis.



Scheme 1. Chemical transformations carried out in this work for complexes **1**-**3**.



Scheme 2. Chemical transformations carried out in this work for complexes **4-6**.

The *solventless* route can be attained either by:

i) *Sublimation*, which occurs gradually starting with transformations at the surface before proceeding to the rest of the bulk solid, accompanied by increasingly intense color changes from white to yellow initially then orange and maroon with time elapsed -- as pyrazine vapor diffuses to the less volatile solid the cyclic trinuclear $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ complex over a time scale of 20 minutes needed to attain complete quenching of the copper trimer's luminescence concomitant with no additional color changes besides those attained progressively since the start of the reaction (Scheme 1); or by:

ii) *Mechanical grinding*, which can accelerate the solventless reaction to start occurring *instantly* and attains complete quenching of the $[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ luminescence in a minute time scale to obtain the final product.

Similar to the situation in all synthetic routes for most complexes, however, the solventless and solvent-mediated transformations attain crystalline products of **1** with powder X-ray diffraction (PXRD) patterns different from one another or that of the simulated PXRD pattern for the single crystals. Thus, Figure 1 shows that both the solventless and the solvent-mediated powders are highly crystalline yet their PXRD is distinctly different from one another or the crystallographic product; the PXRD patterns of all three samples of **1** shown in Figure 1 also shown absence of peaks characteristic of the starting copper precursor, suggesting a complete chemical transformation of each. The fact that there is no coincidence between any of the major PXRD peaks of either powder with those for the single crystal sample also suggests that *crystallization* represents a fourth synthetic variable for the chemical transformations herein.

The solvent-mediated transformation to attain **2** was carried out in an attempt to obtain a mixed-metal/mixed-ligand coordination polymer, upon mixing pyrazine with both the copper $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and silver $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ cyclotrimers, to instead form a purely copper-based metal composition in MOF-TW1. Thus, the formation of MOF-TW1 is sensitive to the synthetic route. Presently, this product has been attained only in the presence of the silver cyclotrimer analogue, as adding that to the reaction mixture did not attain a mixed-metal product. We are currently investigating a possible synthetic route for MOF-TW1 upon using only Cu precursors without silver; multiple attempts to do so have not succeeded thus far. Even more extremely, starting with a silver product, **4**, followed by addition of the $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ precursor results in complete transmetallation whereby all metal content is represented by copper instead of silver or mixed copper/silver in the solid product **3**. Besides transmetallation, rearrangement has taken place whereby all three Cu centers were interconnected by coordination of the bridging Pyz ligands to form a coordination polymer in **3**, whereas this was the case in only two out of the three Ag centers in the asymmetric hexanuclear cluster **4**. Consistent with these observations is a competition solventless experiment we have carried out to further understand the reactivity preference for pyrazine toward copper versus silver. Thus, pyrazine solid was placed in between the orange-emitting $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and green-emitting $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$•benzene solids in a closed container. The solid-state luminescence was monitored as a function of diffusion time of Pyz vapor that sublimes from its solid state. As time elapsed, the copper trimer's photoluminescence quenched in addition to gradual discoloration of its white powder, whereas neither the luminescence nor the white color of the silver trimer undergo any changed to the naked eye. This solventless experiment reinforces the greater reactivity of Pyz with Cu(I) than Ag(I) surmised by the solvent-mediated reactions to attain **2** and **3** instead of mixed-metal products.

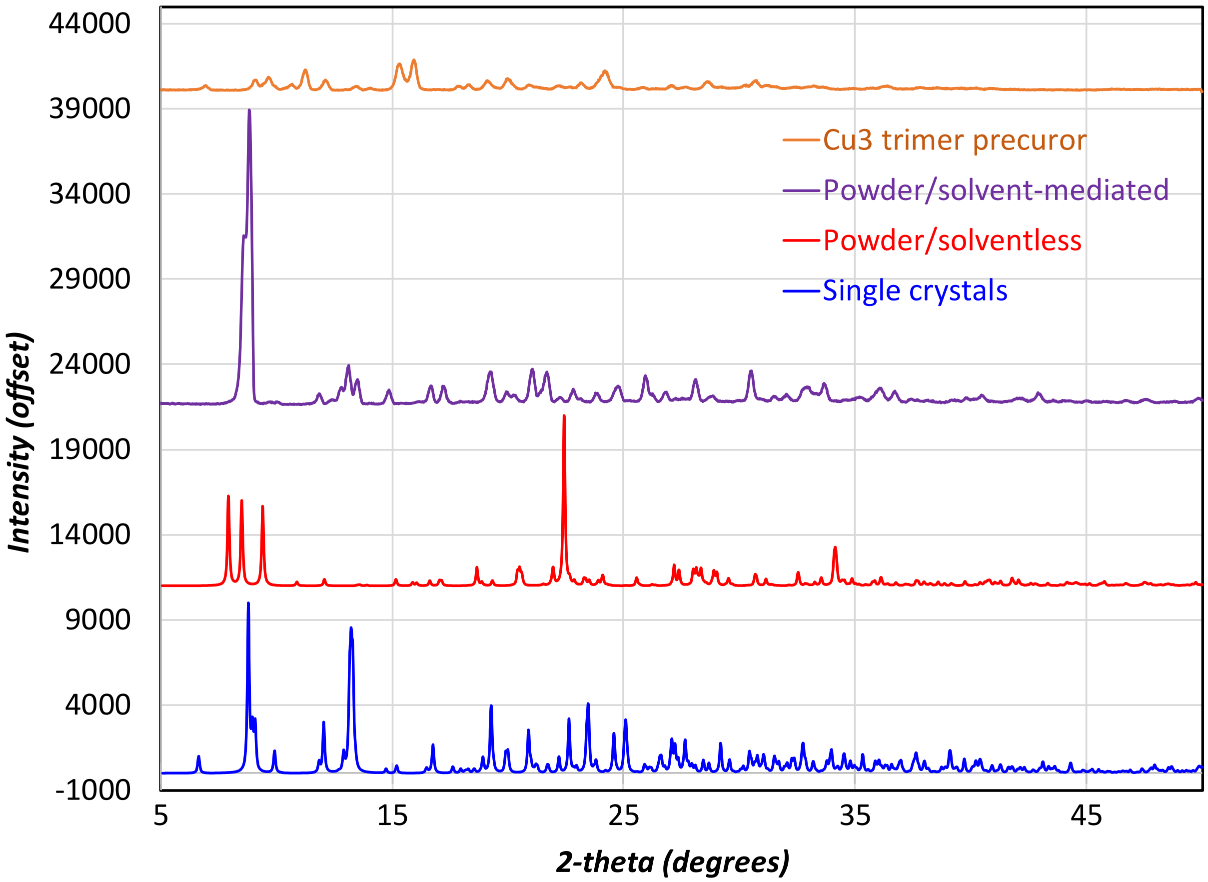


Figure 1. PXRD patterns for **1** in various solid forms versus one another and the copper precursor.

As for the silver products, we have obtained two mixed-ligand products upon solvent-mediated or solvent-free reactions of the $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ cyclotrimer precursor with either the unsaturated/aromatic diimine (pyrazine) or the saturated diamine congener thereof (piperazine) to yield **4** and **5**, respectively. Although both are white products, only the former exhibits detectable luminescence at ambient temperature (vide infra) while the formation of the latter can be followed if the benzene solvate of the cyclotrimer precursor, $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$•benzene, was used; see Scheme 2. The ultimate crystallographic products of the two complexes differed in coordination geometry, attaining a mixed 2-coordinate/3-coordinate geometry in **4** vs a uniform 3-coordinate geometry in **5**. While both crystallographic products deviated from the 3:1 mixing stoichiometry of the neutral bidentate bridging ligand to the $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ cyclotrimer precursor, the coordination was less saturated in **4** than in **5**. Thus, two cyclotrimers are bridged by only two pyrazine molecules in **4** to afford a 1:1 Pyz:Ag_3 (i.e., 1:3 Pyz:Ag) stoichiometric ratio in the crystallized hexanuclear cluster product **4**, leaving two Pyz equivalents unreacted, given that the Pyz:Ag_3 mixing ratio in the reaction was 3:1. Pyrazine molecules coordinate to only four out of the six Ag(I) centers in the dimer-of-trimer with a minimal disruption of the cyclotrimer geometry in the hexanuclear cluster crystalline product **4**. In **5**, on the other hand, piperazine molecules coordinate to all Ag(I) centers and alter the nuclearity of the cyclotrimer precursor to form tetranuclear centers instead. This results in a coordination polymer with interconnected 3-coordinate Ag(I) centers in **5**. The stoichiometric ratio in the product is 1:2 Ppz:Ag, corresponding to half the Ppz molecules from the 1:1 mixing ratio remained unreacted. Thus, among the five crystalline products obtained in $M_3Pz^F{}_3$ (M= Cu or Ag) reactions of LL (Pyz or Ppz) carried out with 1:1 LL:M mixing stoichiometry, three degrees of coordination saturation were obtained in the crystalline product in the order:

2 (1:1 Pyz:Cu) > **1** (1:2 Pyz:Cu) = **3** (1:2 Pyz:Cu) = **5** (1:2 Ppz:Ag) > **4** (1:3 Pyz:Ag)

The greater reactivity of Pyz with Cu(I) than with Ag(I) has been explained earlier in view of experimental observations, whereas we speculate that the greater reactivity of Ppz than Pyz toward silver is in part due to Ppz being a better σ-donor than Pyz. Although Pyz is a good π-acceptor, which would strengthen its bonds with metal centers capable of π back-bonding than the case of a pure σ-donor, Ag(I) is a rather poor π-donating metal center due to its high ionization potential or promotion energy in its monovalent $4d^{10}$ configuration.[23] This attribution also explains the greater reactivity of Cu(I) than Ag(I) toward Pyz from a theoretical perspective.

The PXRD data shown in Figure 2 suggest that the initial powders obtained for **4** are crystalline with better crystallinity for the solventless product, as evidenced by stronger and better-resolved peaks. Indeed, there is coincidence between the solventless powder PXRD peaks with those for both the solvent-mediated powder and the simulated powder pattern of the single crystals, possibly suggesting simultaneous presence of two polymorphs in the solventless product. Similar to the situation in **1**, the PXRD patterns of all three samples of **4** shown in Figure 2 also show absence of peaks characteristic of the starting silver precursor, suggesting a complete chemical transformation of each reaction route.

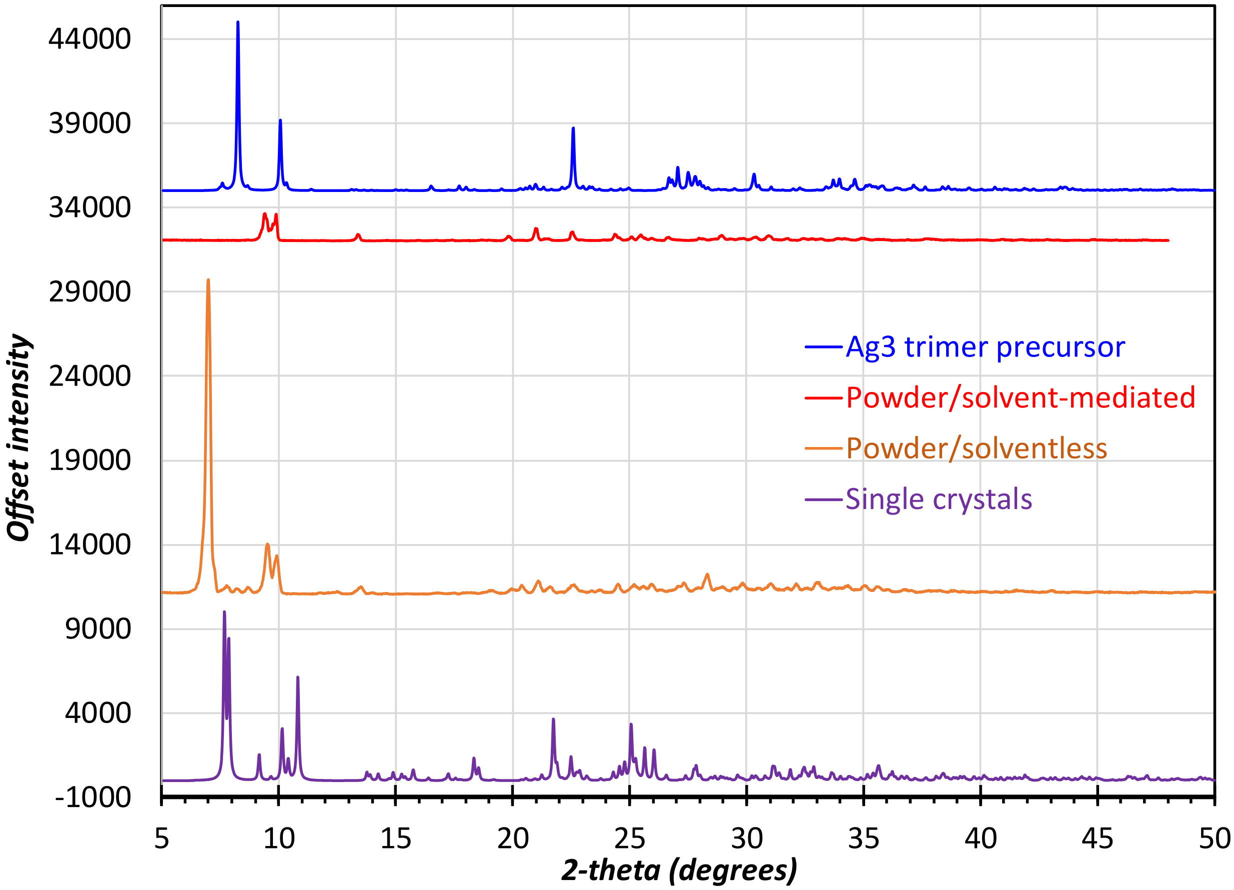


Figure 2. PXRD patterns for **4** in various solid forms versus one another and the silver precursor.

The last product in this work, **6**, was synthesized to investigate the coordination chemistry and optical properties herein for single-chromophoric-ligand reactions (i.e., with only the neutral aromatic diimine versus both diimine and pyrazolate) to attain an ionic instead of neutral product. Indeed, the results have demonstrated the advantage of solventless transformations in this particular case over solvent-mediated reactions in attaining stable Cu(I) products. Thus, starting with the $[Cu(MeCN)_4]BF_4$ precursor instead of the pyrazolate cyclotrimer, adding two equivalents of pyrazine in a closed vessel attains a yellow product upon vapor diffusion of pyrazine from its solid form into the copper precursor at ambient conditions; mechanical grinding also attained the same product. In contrast, when the reaction was attempted under solvent-mediated conditions, an unstable Cu(I) product was attained that quickly underwent oxidation. Crystal growth, however, was possible from acetonitrile for the solventless product to attain the 4-coordinate cationic coordination polymer, **6**. Each pyrazine is shared between two adjacent Cu(I) centers in the coordination polymer, hence giving rise to a 1:1 Pyz:Cu ratio in the crystallized product instead of the 2:1 mixing ratio.

As in the two previous illustrations for **1** and **4**, the powder and single crystals of **6** produced different PXRD patterns; see Figure 3. However, there was a greater resemblance of the PXRD pattern for the powder to the corresponding single crystal pattern for the situation in **6** herein, as seen via overlap of several major peaks, versus the situation for **1** or **4**, suggesting that powder **6** probably includes the crystallographic product plus only traces of other products and/or starting materials – which is the best situation in this regard among all six products. Solvent-free transformations are notorious for their hardship to attain single-crystal-quality products so the common approach has been to combine their PXRD with computer simulations to solve the structure.[11,12] Here we have opted to use both the solventless and solvent-mediated transformations to obtain the crude products whereas we use conventional crystal growth methods for single-crystal analysis of the same product (as in **6**) or different (**1-5**) related ones.

To conclude the discussion of the reactivity in this work, we wish to point out that attempts to isolate piperazine products of Cu(I) have failed, leading to unidentifiable oxidized products. Thus, we conclude that Cu(I) is more compatible with unsaturated/aromatic diimine (pyrazine and pyrazolate) than saturated diamine (piperazine) ligands while the latter can stabilize Ag(I) instead, as manifested by product **5**.

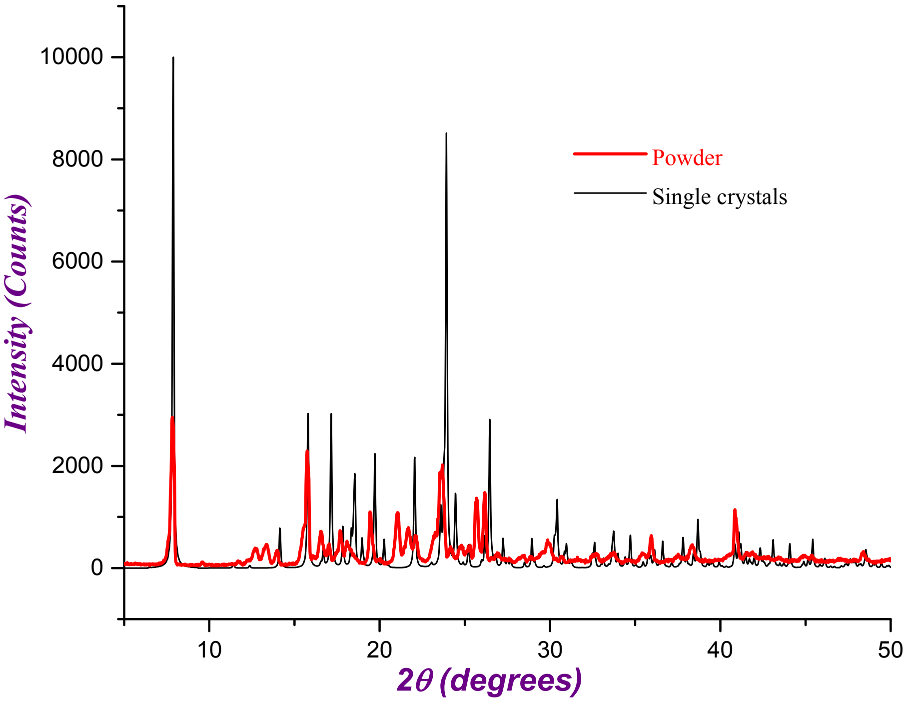


Figure 3. PXRD patterns for powder (at room temperature) vs single crystal (at 200 K) samples of **6**.

Crystal structures of complexes 1–6: Single-crystal X-ray diffraction analysis results are summarized in Tables 1 and S1 (Supporting Information) for the crystal data and important coordination geometry parameters, respectively, whereas Figures 4-9 illustrate the molecular and packing structures of the six complexes. Crystallographic analysis reveals that only **4** is a macrocyclic oligomer (hexanuclear cluster) whereas all five other complexes are coordination polymers (CPs). Among the CPs, only **2** has a MOF structure. The five Pyz-containing structures seem to be strongly stabilized by π-stacking interactions in various modes of sandwiched conformations with various degrees of slipping angles. The limiting cases are manifest by complexes **1** (or **3**) on the one hand -- for a near-perfect sandwiched to maximize π···π molecular orbital overlap -- vs **6** on the other hand for a slipped-stacked arrangement M-N···π/edge···center dipole-quadrupole to maximize electrostatic interactions, respectively.

Complexes **1-4** all crystallize in the triclinic crystal system with the space group $P\bar{1}$. Perspective views of the molecular and packing structures of **1-3** are shown in Figures 4-6, respectively. In complex **1**, copper(I) coordinates to two nitrogen atoms from different pyrazolate ligands and one nitrogen from the pyrazine ligand to form a trimer with three-coordinate metal centers. Unlike $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$, which shows intertrimer Cu···Cu contacts (closest at 3.232 Å),[24] complex **1** does not have intertrimer cuprophilic interactions between copper atoms because the pyrazine acts as a bridging ligand that blocks the interactions between adjacent copper atoms. Since the pyrazolate and pyrazine ligands do not coordinate to the Cu(I) center in a symmetric mode and the hindrance of the three *N*-donor moieties is non-uniform, the three distances of Cu-N are consequently non-identical and so are the bond angles in the coordination spheres, which vary as 131.04(11), 119.72(11), and 109.01(11)°. This observation is consistent with the CuN_3 core being a distorted tetragonal planer structure. Complex **1** is a coordination polymer linked by a molecule of pyrazine to form a 2D network (Figure 4).

Table 1. Crystallographic Data for Complexes **1**-**6**.

Complex	**[1]•CH_2Cl_2**	**[2]•toluene**	**[3]•1.5benzene**	**[4]•2benzene**	[5]	[6]
CCDC	1821487	1821694	1821488	1821489	1821705	1821704
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Formula	$C_{43}H_{20}Cl_2Cu_6F_{36}N_{18}$	$C_{25}H_{18}Cu_2F_{12}N_8$	$C_{30}H_{18}Cu_3F_{18}N_9$	$C_{50}H_{26}Ag_6F_{36}N_{16}$	$C_{14}H_{12}Ag_2F_{12}N_6$	$C_8H_{10}BCuF_4N_4$
Formula weight	1924.91	785.55	1037.15	2182.09	708.04	312.55
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C_{2/c}$	P_{bca}
a, (Å)	11.023(5)	9.8425(5)	11.9433(6)	10.537(4)	15.056(2)	10.709(2)
b, (Å)	11.174(5)	12.2763(6)	13.2270 (6)	11.355(4)	27.738(3)	10.614(2)
c, (Å)	14.641(11)	13.2130(6)	15.0253 (11)	15.527(5)	12.0564(14)	22.430(4)
α, (deg)	103.763(12)	83.306(1)	98.870(1)	98.364(5)	90	90
β, (deg)	104.969(11)	85.895(1)	108.650(1)	105.997(5)	121.855(2)	90
γ, (deg)	106.907(8)	75.710(1)	116.392(1)	106.056(5)	90	90
V, ($Å^3$)	1568.2(16)	1535.05(13)	1887.8(2)	1666.0(9)	4276.8(9)	2549.6(7)
Z	1	2	2	1	8	8
T, (K)	100(2)	200(2)	200(2)	200(2)	100(2)	220(2)
λ, (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}, (Mg/m^3)	2.028	1.700	1.825	2.175	2.199	1.629
μ, (mm^{-1})	2.241	1.490	1.801	1.880	1.950	1.748
Crystal size, (mm^3)	0.20 x 0.08 x 0.08	0.22 x 0.14 x 0.03	0.36 x 0.23 x 0.11	0.32 x 0.13 x 0.12	0.21 x 0.20 x 0.07	0.12 x 0.10 x 0.09
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Abs. Corr. factor	0.8446/0.6590	0.9637/0.7343	0.8293/0.5641	0.8045/0.5837	0.8837/0.6883	0.8530/0.8151
Total reflections	14320	15834	25717	15589	28523	25124
Independ. Reflections	6247	6782	8298	7118	4718	2747
Data/res/parameters	6247 / 0 / 484	6782 / 0 / 425	8298 / 0 / 541	7118 / 9 / 503	4718 / 0 / 315	2747 / 0 / 165
R_1 [I > 2σ(I)]	0.0365	0.0343	0.0424	0.0649	0.0201	0.0258
wR2 [I > 2σ(I)]	0.0940	0.0873	0.1199	0.1590	0.0601	0.0757
R_1 (all data)	0.0475	0.0494	0.0531	0.0898	0.0220	0.0353
wR_2 (all data)	0.1022	0.0950	0.1291	0.1831	0.0621	0.0820
GOF on F^2	1.043	1.032	1.032	1.032	1.023	1.028
Δρ(max), Δρ(min) (e/$Å^3$)	1.338, -1.351	0.517, -0.489	1.005, -0.639	1.805,-1.822	1.064, -0.679	0.239, -0.389

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - wF_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$

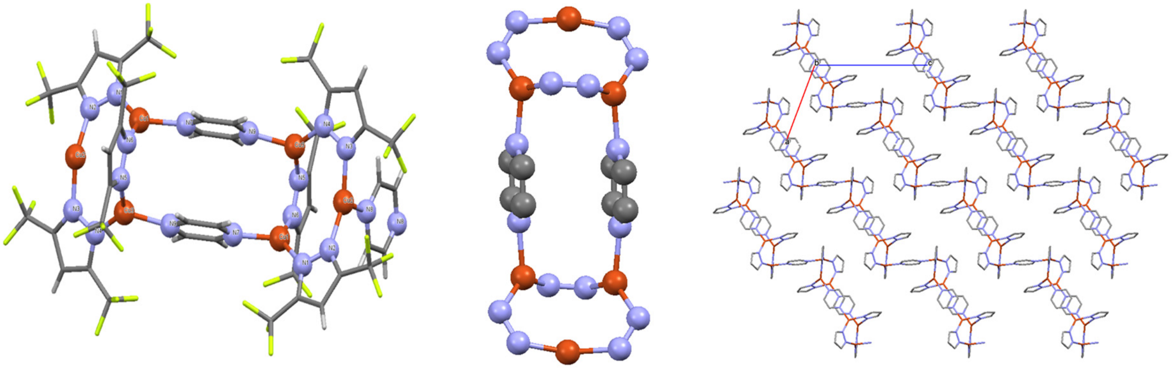
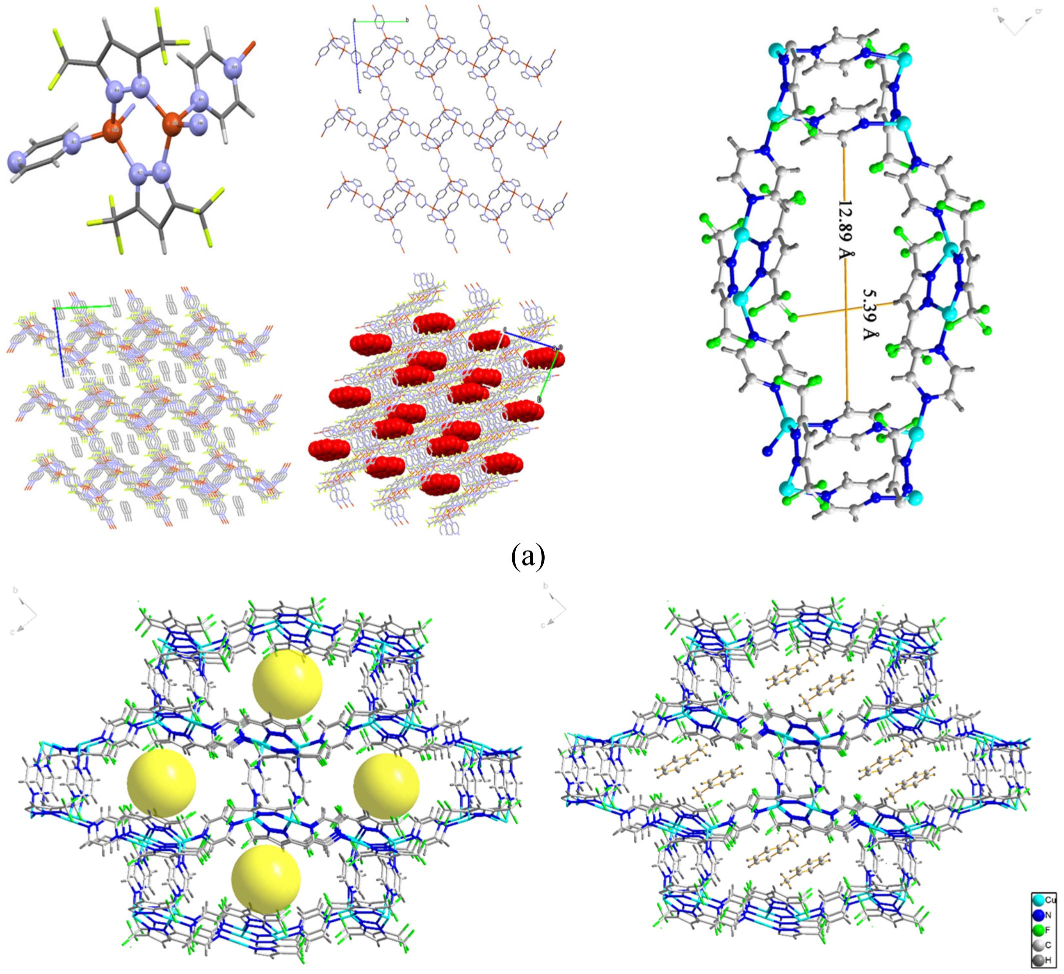


Figure 4. Molecular and packing structures of $\{Cu_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_3{\bullet}CH_2Cl_2\}_\infty$ (**1**$\bullet CH_2Cl_2$).

In the crystal structure of complex **2**, each Cu(I) atom coordinates to two N-atoms from two different pyrazolate ligands, plus two other N-atoms from two different pyrazine ligands to form a dimer with four-coordinate metal centers. Such dinuclear units are further linked by pyrazine to form a 3D network structure (Figure 5). Indeed, complex **2** is a toluene adsorption adduct of a metal-organic framework we dub “MOF-TW1” akin to the partially-fluorinated “MOFFs” class described by Miljanić and co-workers.[25] The pore characteristics include the following features: a) total potential solvent-accessible volume is 416.4 $Å^3$, representing 27.10% of the 1535.05(13) $Å^3$ unit cell volume, as calculated by Platon; b) surface area = 1278 m^2/g, as calculated by Materials Studio; and c) pore size of ~ 13.9 Å × 5.4 Å, as measured by Mercury, corresponding to the dimensions of the parallelogram-shaped channel cross sections (as shown in Figure 5a, whereas the yellow spheres in Figure 5b exhibit a diameter that corresponds to the 5.4 Å shorter distance). Efforts to activate MOF-TW1 and study its adsorption characteristics will be made and described elsewhere, when we attempt and succeed in synthesizing a large crystalline powder batch (beyond the small single crystal batch herein) with the same powder XRD pattern as that of the simulated patter for the single crystals of this porous phase. This will be unlike the present situation whereby the bulk powder batch isolated clearly does not correspond to the single crystals of MOF-TW1 (Figure 2 per XRD evidence, in addition to the visual evidence based on the solid color, as illustrated in Scheme 1). Such efforts are beyond the scope of this manuscript – which instead focuses on the versatility of the supramolecular structures and corresponding colorimetric/optoelectronic properties thereof for the various coordination polymers and cluster oligomers to which complex $\{(\mathbf{2}\bullet\text{toluene})\}_\infty$ belongs.



(a)

(b)

Figure 5. (a) Molecular, packing structures, and pore cross section of $\{Cu_2[3,5\text{-}(CF_3)_2Pz]\}_2(Pyz)_2\bullet\text{toluene}\}_\infty$ ($\mathbf{2}\bullet$toluene = MOF-TW1). (b) Pore representation of solvent-accessible regions (yellow spheres in evacuated/left and toluene-occupied/right crystals) of MOF-TW1.

Complex {(**3**•benzene)}$_\infty$ is rather similar to complex {(**1**•CH_2Cl_2)}$_\infty$ (see Scheme 1, Figure 6 vs Figure 4, and Tables 1-2). The two CPs exhibit interconnected trinuclear units whereby each Cu(I) center becomes 3-coordinate (vs 2-coordinate in the cyclotrimer precursor) by virtue of two Pyz bridging units connecting two Cu atoms on one side of each Cu_3 triangle to two opposing Cu atoms in the next triangle while, likewise, the third Cu atom on the vertexes of adjacent triangles are connected by another Pyz bridge. However, besides the difference in the solvate constitution, the propagation of the CP chain occurs linearly in **3** vs a zigzag manner in **1**. In complex {(**4**•benzene)}, only two of the three Ag(I) atoms in adjacent Ag_3 triangles form 3-coordinate centers due to side connection, similar to the situation for the Cu atoms in complex **1** or **3**, but without extended-chain formation to, instead, form a hexanuclear dimer-of-trimer, as the third Ag atoms in opposing triangle vertexes remain 2-coordinate as in the cyclotrimer precursor -- without Pyz bridging (Figure 7).

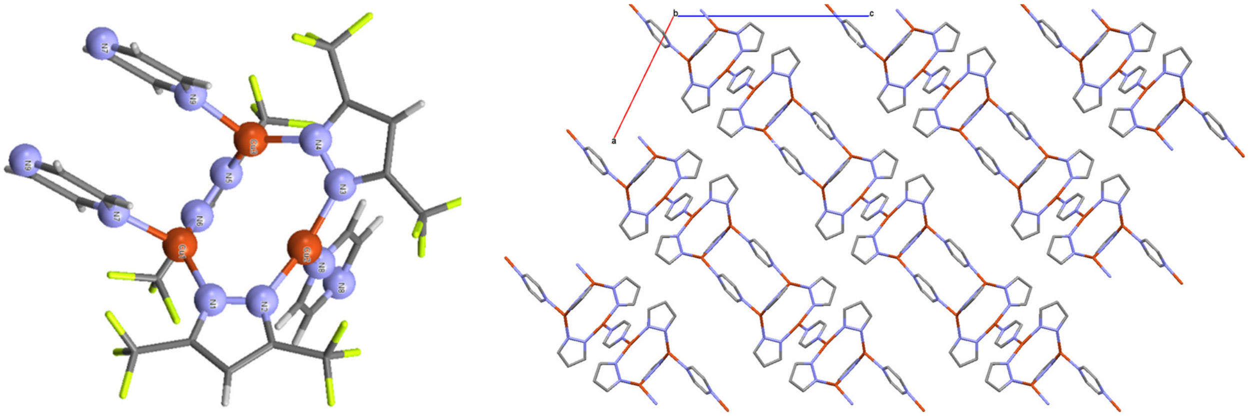


Figure 6. Molecular and packing structures of {$Cu_3[3,5\text{-}(CF_3)_2Pz]_3(Pyz)_{1.5}$•1.5benzene}$_\infty$ (**3**•1.5benzene).

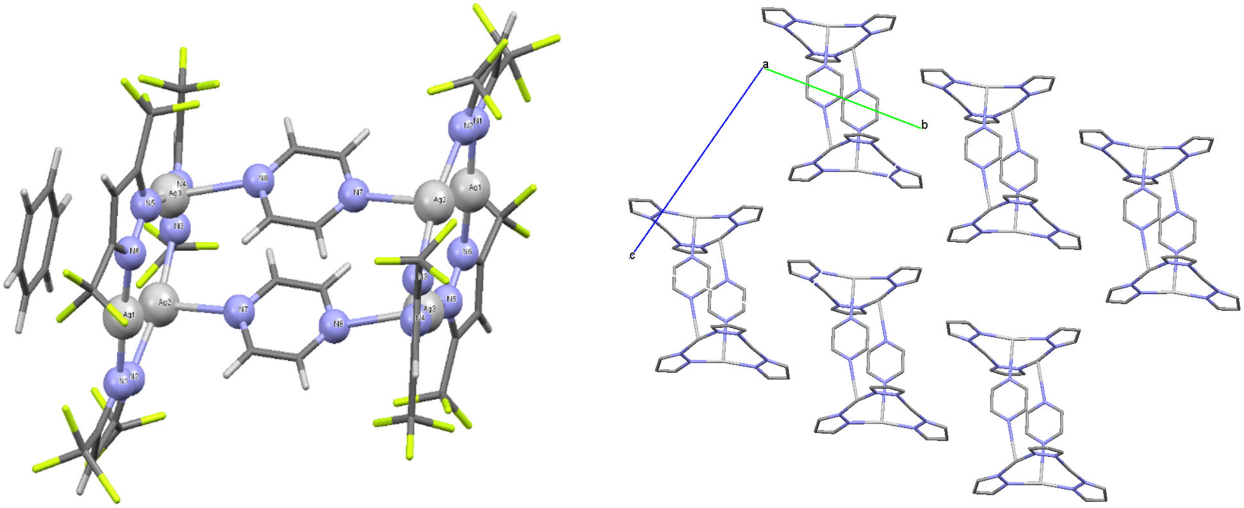


Figure 7. Molecular and packing structures of $\{Ag_6[3,5\text{-}(CF_3)_2Pz]_6(Pyz)_2\bullet 2\text{benzene}\}$ (**4**•2benzene).

Complex **5** crystallizes in the monoclinic crystal system with the space group $C_{2/c}$, whereby interconnected tetramers are bridged by the saturated Ppz ligands. Ag(I) coordinates to two N-atoms from the pyrazolate ligands and a third N-atom from the piperazine ligand to form a tetranuclear cluster with 3-coordinate metal centers with each two Ag(I) centers on opposite sides of the Ag_4 molecular square expanding the structure of complex **5** into infinite zigzag chains (Figure 8 and Scheme 2), somewhat akin to the situation in complex **1**. While X-ray analysis (insensitive for H atoms) and ^{1}H NMR (due to deuterated acetonitrile solvent interference) cannot directly account for the intuitive presence of the H(N) atoms of piperazine, a secondary amine group was confirmed in the IR spectra of complex **5** with a single peak in the area of 3300 cm^{-1}. (N-H stretches usually exhibit in the 3400-3250 cm^{-1} whereby primary amines usually show two "fangs" while secondary amines show a single peak.) Overall, X-ray crystallographic data for complex **5** show interesting phenomena whereby the planar cyclotrimer precursor changes to a non-planar cyclic tetramer upon the reaction with amine groups of piperazine. Kokunov et al.

confirmed by the crystal structures of $[Ag^{I}(C_4H_{10}N_2)]CH_3SO_3$ and $[Ag^{I}(C_4H_{10}N_2)]PO_2F_2$ the presence of hydrogen bonding between the N–H donors of piperazine and the oxygen atoms of the sulfonate anion, resulting in interactions between alternating anion-cation layers.[1k] The steric factor might be the reason for forming such tetramers like $\{[3,5\text{-}({}^{t}\text{Bu})_2\text{Pz}]\text{Ag}\}_4$, reported by Raptis et al., which is one of the uncommon nuclearities among monovalent silver (or, in general, d^{10} coinage metal) pyrazolates.[26]

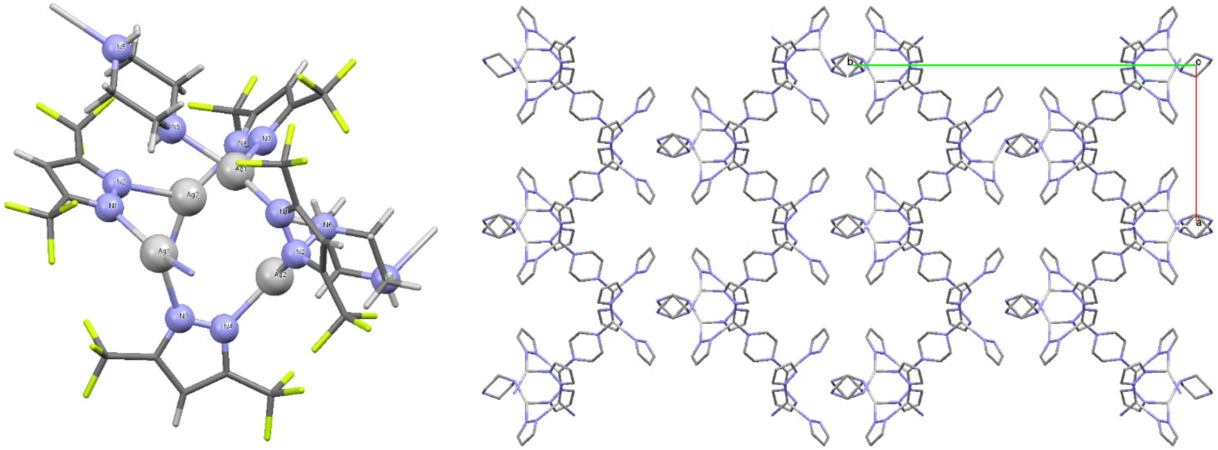


Figure 8. Molecular and packing structures of $\{Ag_2[3,5\text{-}(CF_3)_2Pz]_2(Ppz)\}_\infty$ (**5**).

Complex **6** crystallizes in the orthorhombic system with the P_{bca} space group, whereby repeat units are mononuclear complexes. Copper (I) coordinates to two nitrogen atoms from pyrazine and two nitrogen atoms from acetonitrile to form a monomer with four coordinates. The four distances of Cu-N are not exactly the same and likewise for the angles around copper atoms in the coordination sphere (varying within 1.945–2.104 Å and 104.8–129.7°, respectively; see Table S1, Supporting Information) – consistent with the CuN_4 core exhibiting a distorted tetrahedral structure (Figure 9). Two molecules of acetonitrile coordinate to Cu(I) atoms to reduce the steric hindrance, whereas the two pyrazine molecules extend the coordination infinitely into interpenetrating twisted networks of overlapping zigzag chains (to plug any significant pore formation otherwise).

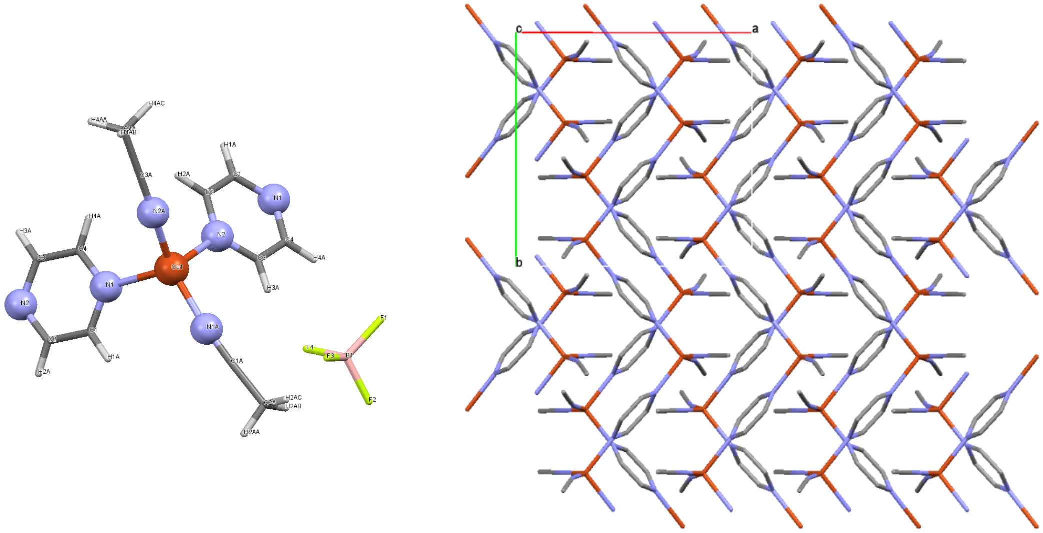


Figure 9. Molecular and packing structures of $\{[Cu(Pyz)(MeCN)_2][BF_4]\}_\infty$ (**6**).

Photoluminescence data: Considering the interesting photophysical properties displayed by $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$,[15h-i] a thin film of the copper trimer precursor $[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ was cast onto a quartz tube by dissolving a small amount in benzene and adding a few drops to the tube followed by drying on a hot plate. The photoluminescence (PL) of the copper trimer was measured during the exposure of the solid pyrazine in a closed system. The quenching of the copper trimer's bright-orange PL ($\lambda_{max} \sim 550$ nm) was monitored versus reaction time with pyrazine. The orange PL quenches instantly -- as soon as pyrazine is introduced to the thin film (Figure 10).

Complex **4** exhibits blue PL in the solid state at room temperature (RT) and green PL in the solid state at 77K (Figure 11). However, it does not exhibit any PL in solution. The photoluminescence excitation (PLE) band, with maximum peak at λ_{exc}= 334 nm, and the emission band, with maximum peak at λ_{em}= 483 nm, were observed for the solid (crystalline powder) at RT. The RT emission lifetime is 30.5 µs, while the 77K emission lifetime is 106 µs, suggesting phosphorescence from a triplet-excited state.

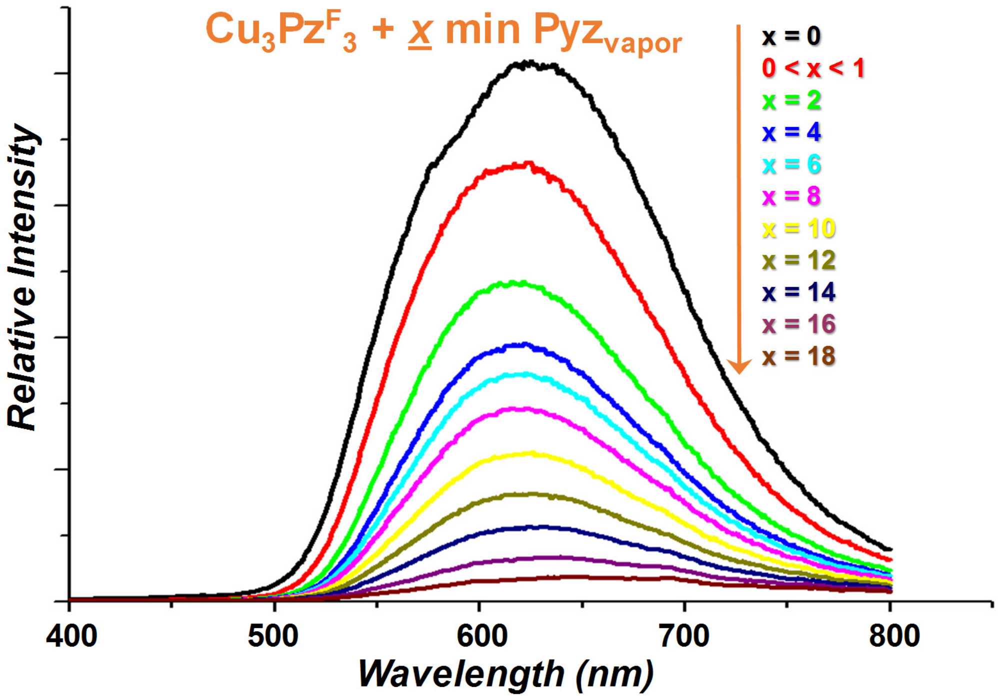


Figure 10. Photoluminescence quenching experiment of copper trimer $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ versus reaction time with solid pyrazine as it sublimes.

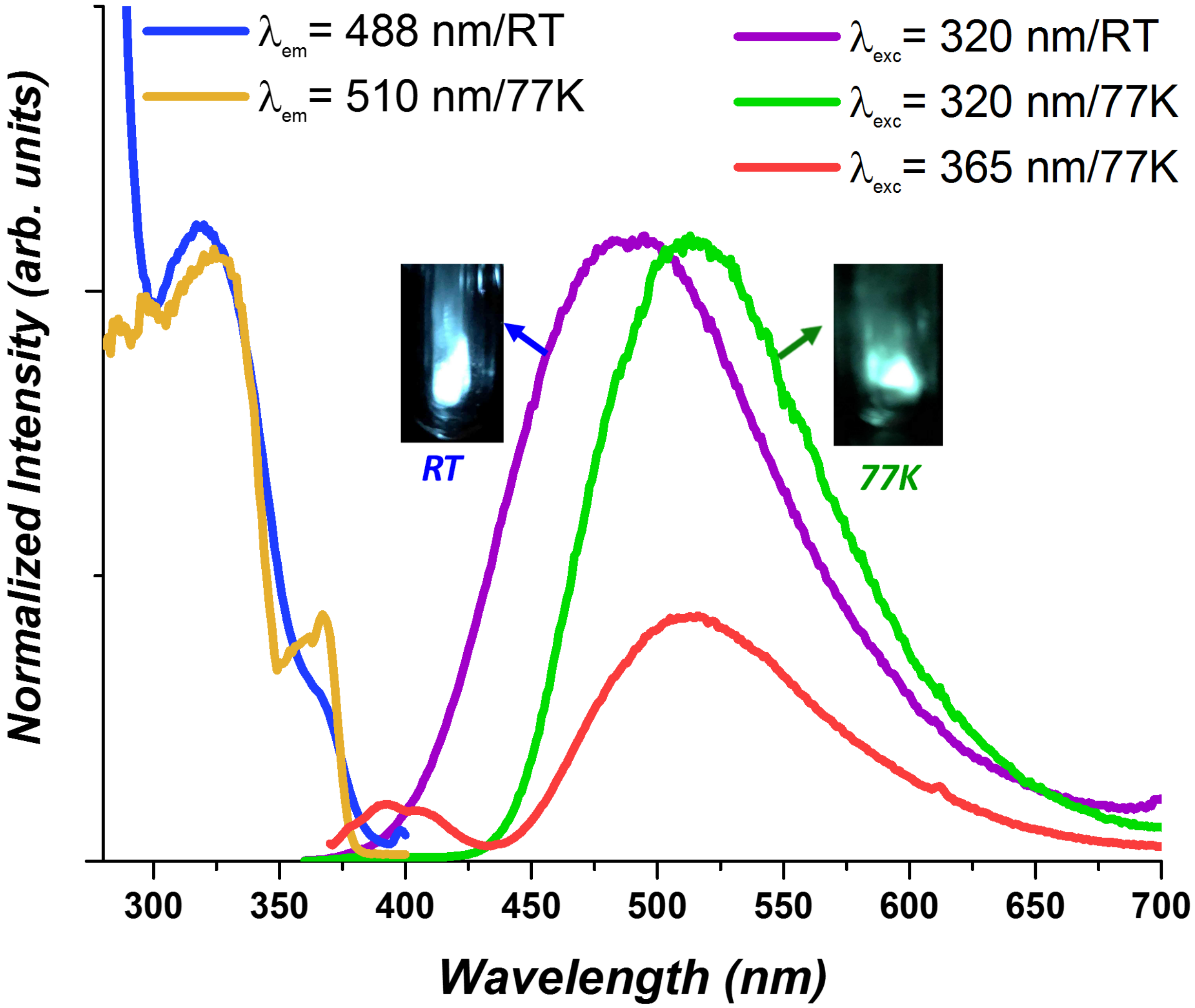


Figure 11. Photoluminescence excitation (left) and emission (right) spectra of complex **4** in the solid state at RT (top) and 77 K (bottom). The traces are normalized based on the excitation spectra while the apparent weak emission at ~ 400 nm is an artifact from the long-pass filter material.

Conclusions

In this work, we describe the synthesis, crystal structures, and photophysical properties of six new coordination compounds of Cu(I) or Ag(I) with *N*-donor linearly-bridging bidentate diimine or diamine ligands. Of those products, five coordination polymers and one polycyclic oligomeric cluster were obtained. Three polymorphs or constitutional isomers of the same Cu(I)/mixed-ligand (pyrazine and 3,5-tris(trifluoromethyl)pyrazolate) composition were obtained upon different synthetic variables (solventless reactions via vapor diffusion or mechanical grinding, solvent-mediated transformations, including transmetallation, varying crystal growth conditions, etc.). Among the five coordination polymers, one was a metal-organic framework **(**MOF-TW1) with a surface area and void volume of ca. 1300 m^2/g and 24%, respectively. Reactions have not always attained the targeted products such that copper-only coordination polymers were obtained upon two reaction attempts that have targeted mixed-metal products. In particular, reactions involving an aromatic diimine indicate greater affinity and reactivity to Cu(I) than Ag(I), whereas the latter is more reactive toward the aliphatic diamine analogue – presumably due to its poor π-acceptance ability. Changes in the metal precursor as well as the *N*-donor ligand have drastically altered the structural and photophysical properties. Among the crystallographic six products, three exhibit a uniform 3-coordinate, two uniform 4-coordinate, and one mixed 2-coordinate/3-coordinate metal centers. All Cu(I) products are colored and non-luminescent, allowing the monitoring of their formation by gradual color change to discolor the reactants and/or by quenching the luminescence of the phosphorescent precursor. On the other hand, the Ag(I) products are colorless but luminescent when an aromatic bridging diimine is used, allowing the monitoring of the product formation by gradual turn-on of its phosphorescence, whereas the non-luminescent product can be monitored by disappearance of the luminescence of a solvated precursor. The work includes aspects toward integration of "green chemistry" into the inorganic synthesis of optoelectronic and porous functional materials based on d^{10} complexes by carrying out a series of solvent-free reactions to obtain the crude product. These reactions complement solvent-mediated reactions in the assembly or disassembly of the reactants and products, suggesting the worthiness to pursue and expand the solventless chemistry of d^{10} coordination compounds. Both vapor diffusion and mechanical grinding have been used under ambient laboratory conditions to carry out chemical transformations that could be monitored by the human eye as the reaction progresses, as observed by gradual color/intensity changes detectable by the human eye under room or UV light.

Experimental Section:

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Dried and purified, ACS reagent grade benzene was used as a solvent to carry out the synthesis. $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_{3,}$[19] $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_{3,}$[19] and $[Cu(MeCN)_4]BF_4$ [20] were prepared according to the published procedures. ^{1}H-NMR spectra were recorded at 25°C on a Varian 400 spectrometer; the proton chemical shifts were reported in ppm versus dichloromethane and acetonitrile. IR spectra were recorded at 25°C on a Shimadzu FTIR spectrometer. Elemental analysis was performed at Intertek Pharmaceutical Services – Whitehouse, NJ. Thermogravimetric analysis (TGA) was performed at 25°C on a TA Q50 TGA analyzer.

Spectroscopic Measurements. Steady-state photoluminescence spectra were acquired with a PTI QuantaMaster Model QM-3/2006SE scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The emission spectra were corrected for the detector wavelength-dependent response. The excitation spectra were also corrected for the wavelength-dependent lamp intensity. Temperature-dependent studies were acquired with an Oxford optical cryostat using liquid nitrogen as coolant. Lifetime data were acquired using a high speed pulsed xenon lamp source interfaced to the PTI instrument along with an autocalibrated "QuadraScopic" monochromator for excitation wavelength selection.

X-ray Crystallographic Data. Crystal structure determination for compounds **1-6** were carried out using a Bruker SMATR APEX2 CCD-based X-ray diffractometer equipped with a low temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). For the complex **1, 5** measurements were taken at 100(2) K, for **2-4** at 200(2)K and for **6** at 220(2) K. Data collection, indexing, and initial cell refinements were carried out using APEX2,[27a] frame integration and final cell refinements were done using SAINT.[27b] An absorption correction was applied using the program SADABS.[27c] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the compounds **1-6** were placed in idealized positions and were refined as riding atoms. Structure solution, refinement, graphic and generation of publication materials were performed by using SHELXTL software.[27d]

Synthesis of 1. Both *solventless* and *solvent-mediated* transformations attained this product. One *solventless* route entailed a 1:3 molar ratio of $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ (0.1 g) and pyrazine (0.034 g) being mixed in a closed vial where they were left to react. Due to the fact that pyrazine sublimes as well at room temperature and ambient pressure, it reacts in the gas phase via the vapor of its solid with the less volatile $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ cyclotrimer solid, resulting in a color change of the white copper trimer immediately to yellow, orange, and ultimately maroon – gradually as time goes by. The reaction starts occurring in a minute time scale and takes approximately 20 min to completion. The solventless route can be further accelerated by mechanical grinding of the same stoichiometric amounts, whereby the reaction starts occurring *instantly* and is completed within a minute time scale. The maroon product obtained was very soluble in acetone and acetonitrile, among other common organic solvents. Finally, the solvent-mediated route involved the reaction of a 1:3 molar ratio of $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ (0.097 g) and pyrazine (0.0336 g) in 10 mL of benzene. The solution color changed immediately to orange. The resulting product was obtained by removing the solvent under reduced pressure and further dried by vacuuming for extra 2 hrs. X-ray quality crystals were obtained from hot benzene/dichloromethane. M.p. 180 °C. ^{1}H-NMR using as reference acetonitrile d$_3\delta$ resulted in the following resonances: 6.98 ppm (Pz^F, C-H), 8.70 ppm (Pyz, C-H). IR: 2134.15 cm^{-1} (C=N stretch), 1940.45 cm^{-1} (aromatic C=C bend), 1509.64 cm^{-1} (aromatic C-C stretch), 3094.25 cm^{-1} (aromatic C-H stretch). Anal. Calcd. for $C_{42}H_{18}Cu_6F_{36}N_{18}$: C, 27.42; H, 0.99; N, 13.70%. Found : C, 27.07 ; H, 0.81; N, 13.35 % (without dichloromethane).

Synthesis of 2. The reaction entailed a 1:1:3 molar ratio of {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ (0.097 g), {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ (0.1 g), and pyrazine (0.0336 g), all mixed in 10 mL of benzene. The color of solution changed immediately to light orange. The reaction was stirred for 6 hours. The resulting product was obtained by removing solvent using vacuum and further dried by vacuuming for extra 2 hours. The product was soluble in most of organic solvents, including benzene and acetonitrile. X-ray quality crystals were obtained from hot toluene. M.p. 160 °C. ^{1}H-NMR using as reference acetonitrile d$_3\delta$ resulted in the following resonances: 7.40 ppm (Pz^F, C-H), 8.70 ppm (Pyz, C-H). IR: 2964.25 cm^{-1} (aromatic C-H stretch), 2049.15 cm^{-1} (C=N stretch), 1695.45 cm^{-1} (aromatic C=C bend), 1519.64 cm^{-1} (aromatic C-C stretch). Anal. Calcd. for $C_{18}H_{10}Cu_2F_{12}N_8$: C, 31.18; H, 1.45; N, 16.16%. Found: C, 30.66; H, 1.37; N, 15.65%. (without toluene).

Synthesis of 3. A 1:1 molar ratio reaction was carried out whereby {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ (0.1 g) and {Ag$_6$[3,5-(CF$_3$)$_2$Pz]$_6$(Pyz)$_2$(benzene)$_2$} (0.27 g -- synthesized following the same procedure below for complex **4**) were mixed in 10 mL of benzene. A light yellow color started to form immediately. The reaction was stirred for 2 hours. The resulting product was obtained by removing solvent using vacuum for 2 hours. The light yellow solid product obtained has no luminescence. The product was very soluble in organic solvents, such as benzene, acetone and acetonitrile. X-ray quality crystals were obtained from hot benzene. M.p. 155 °C. ^{1}H-NMR using as reference acetonitrile $d_3\delta$ resulted in the following resonances: 7.00 ppm (Pz^F, C-H), 8.56 ppm (Pyz, C- H), IR: 2964.25 cm^{-1} (aromatic C-H stretch), 2049.15 cm^{-1} (C=N stretch), 1785.45 cm^{-1} (aromatic C=C bend), 1619.64 cm^{-1} (aromatic C-C stretch). Anal. Calcd. for $C_{24} H_{12} Cu_3 F_{18} N_9$: C, 30.06; H, 1.26; N, 13.14%. Found: C, 30.18; H, 1.34; N, 13.98 % (without benzene).

Synthesis of 4. A 1:3 molar ratio reaction was carried out whereby $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ (0.1 g) and pyrazine (0.028 g) were mixed in dichloromethane (10 mL). The reaction was stirred for 2 hours. The resulting product was obtained by removing solvent using vacuum for 2 hours. The white product obtained has blue luminescence. The product was partially soluble in organic solvents, such as acetonitrile and acetone. X-ray quality crystals were obtained from dichloromethane by slow evaporation. M.p. 170°C. ^{1}H-NMR using as reference acetonitrile $d_3\delta$ resulted in the following resonances: 7.3 ppm (Pz^F, C-H), 8.70 ppm (Pyz, C-H). IR: 3160.06 cm^{-1} (aromatic C-H stretch), 2165 cm^{-1} (C=N stretch), 2170.45 cm^{-1} (aromatic C=C bend), 1972.38 cm^{-1} (aromatic C- C stretch). Anal. Calcd. for $C_{38} H_{14} Ag_6 F_{36} N_{16}$: C, 22.53; H, 0.70; N, 11.06%. Found: C, 21.66 ; H, 0.33; N, 10.70 % (without 2 molecules of benzene).

Synthesis of 5. A 1:3 molar ratio reaction was carried out whereby $\{[3,5\text{-} (CF_3)_2Pz]Ag\}_3$ (0.1 g) and piperazine (Ppz) (0.066 g) were mixed in dichloromethane (10 mL); varying the molar ratio to 1:6 or 1:2 attained the same subsequent observations. The reaction was stirred for 2 hours. The product was collected using vacuum filtration and further dried under vacuuming for 2 hours. The white product obtained has no luminescence. The product was insoluble in most organic solvents, such as benzene and dichloromethane, but it is partially soluble in acetonitrile. Using sonication and filtration was essential to acquire the best result for recrystallization. X-ray quality crystals were obtained from acetonitrile by slow evaporation. M.p. 250 °C (dec.). ^{1}H-NMR using as reference acetone $d_6\delta$ resulted in the following resonances: 7.1 ppm (Pz^F, C-H), 2.85 ppm (Ppz,

$C-H_2$), 1.90 ppm (Ppz, N-H). IR: 3276.73 cm^{-1} (N-H stretch), 3020.98 cm^{-1} (aromatic C-H stretch), 2847.67 cm^{-1} (aliphatic C-H stretch), 2353.23 cm^{-1} (C=N stretch), 1531.90 cm^{-1} (aromatic C=C bend), 1433.83 cm^{-1} (aromatic C-C stretch). Anal. Calcd. for $C_{14} H_{12} Ag_2 F_{12} N_6$: C, 23.75; H, 1.71; N, 11.87%. Found: C, 23.07 ; H, 0.89; N, 11.12 %.

Synthesis of 6. A 1:2 molar ratio reaction was carried out whereby $[Cu(MeCN)_4]BF_4$ (0.1 g) and pyrazine (Pyz) (0.05g) were mixed in a closed vial where they were left to react. Due to the fact that pyrazine sublimes at room temperature, $[Cu(MeCN)_4]BF_4$ reacts with pyrazine in the gas phase resulting in a color change of the white copper precursor immediately to yellow. The product was soluble only in acetonitrile. The yellow product was crystalized using acetonitrile and slow evaporation for 2 days under inert atmosphere using purified nitrogen gas to obtain X-ray quality single crystals. M.p. > 500 °C. ^1H-NMR using as reference acetonitrile $d_3\delta$ resulted in the following resonances: 8.4 ppm (Pyz, C-H). IR: 2102.80 cm^{-1} (C=N stretch), 1976.32 cm^{-1} (aromatic C=C bend), 1592.19 cm^{-1} (aromatic C-C stretch), 3058.43 cm^{-1} (aromatic C-H stretch). Anal. Calcd. for $C_8 H_{10} B Cu F_4 N_4$: C, 30.74; H, 3.23; N, 17.93%. Found: C, 31.04; H, 2.68; N, 17.94.

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Supporting Information Available. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxx.

Additional experimental data referenced in the text (PDF).

Accession Codes CCDC 1821487, 1821694, 1821488, 1821489, 1821705, and 1821704 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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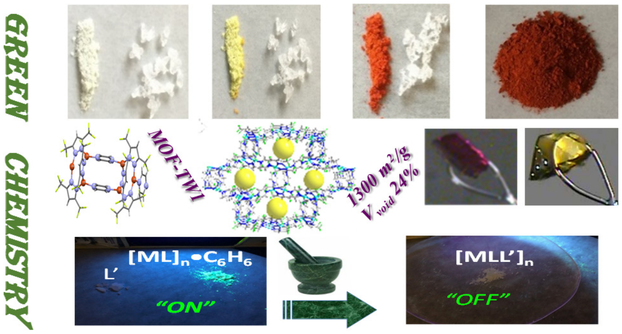

TOC Synopsis: Six Cu(I) and Ag(I) coordination polymers/oligomers are obtained using "green" solventless transformations at ambient temperature/pressure without automated equipment, complementing solvent-mediated processes. Discoloration and/or luminescence on/off switching accompany all reactions. Among the crystallographically-identified products, one hexanuclear cluster and five coordination polymers formed, three of which were polymorphs or constitutional-isomers of the same composition and one was a metal-organic framework **(**MOF-TW1) with a surface area and void volume of ca. 1300 m^2/g and 24%, respectively.