

Anions as Connectors for Higher Dimensions. Silver(I) Trifluoroacetate with 3,3'-Oxybispyridine vs 3,3'-Thiobispyridine

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Trifluoroacetate anion as a connector has been studied on AgCF_3CO_2 compounds with 3,3'-Py₂X (X = O vs S). The reaction of AgCF_3CO_2 with 3,3'-Py₂X (X = O vs S) produces 1 : 1 adducts of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{X})]$. Crystallographic characterization of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$ (monoclinic $P2_1$, $a = 7.383(1)$ Å, $b = 19.801(3)$ Å, $c = 9.297(3)$ Å, $\beta = 100.26(2)^\circ$, $V = 1337.4(5)$ Å³, $Z = 2$, $R = 0.0386$) reveals that the 3,3'-Py₂O spacer connects two silver ions to give a single strand and that the single strands are linked *via* the trifluoroacetate anions in an "up and down even-bridge" to give an elegant molecular grid. The framework of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ (monoclinic $P2_1/c$, $a = 8.331(2)$ Å, $b = 14.010(2)$ Å, $c = 11.926(3)$ Å, $\beta = 93.70(2)^\circ$, $V = 1385.1(6)$ Å³, $Z = 4$, $R = 0.0589$) is a single-strand. The single strands are connected *via* the trifluoroacetate anions in a double-bridge, resulting in a typical molecular chicken-wire. The trifluoroacetate anion as a connector appears to be primarily associated with its moderately coordinating ability. Their structural features have been discussed based on the anion exchangeability. Thermal analyses indicate that the compounds are stable up to approximately 200 °C.

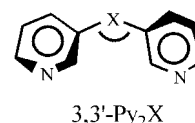
Key Words : Bridged anions, Silver(I) complexes, Bipyridine analogs, Coordination polymers

Introduction

Until recently, rational control of molecular frameworks *via* weakly coordinating (counter)anions has been rare due to the less effective electrostatic binding interactions. Studies on the anionic features such as negative charge, size, a wide range of geometries, significant solvent effects, and pH dependence show that some anions directly and indirectly play crucial roles in the construction of designed molecular buildings.¹⁻⁴ Since anion coordination chemistry emerged as a booming field owing to a timely interest from environmental pollution, industrial chemicals, biological process, ionic liquids, catalysis, lithium battery, and health-related perspectives,⁵⁻⁸ the efficient utilization of anions in the field of molecular construction has been attempted. As a consequence, recent developments on anions include exciting advances in anion template assembly, ion-pair recognition, and various functions in supramolecular chemistry.⁹⁻¹² In this category, some fluorinated anions have been studied for battery technology, ionic liquids, recognition, and catalysis.⁹ We previously reported that the reaction of Ag(I) with chalcogenobispyridine (Py₂X; X = O, S) results in the formation of functional molecular materials.¹³⁻¹⁸ Among various chalcogenobispyridines, 3,3'-oxybispyridine (3,3'-Py₂O) and 3,3'-thiobispyridine (3,3'-Py₂S) have been known to be very interesting spacer ligands. They have similar angular and flexible components that possess non-rigid interannular dihedral angles between two pyridyl groups,¹⁹⁻²¹

but both spacers exhibit delicate differences in the size, lone-pair delocalization, conformational energy barrier, and donating ability.

In order to scrutinize the roles of anions in the self-assembly of AgCF_3CO_2 with 3,3'-Py₂X (X = O, S), we describe the structures and related properties of AgCF_3CO_2 with 3,3'-Py₂O vs 3,3'-Py₂S. Trifluoroacetate (CF_3CO_2^-) is a readily available anion that can coordinate weakly to metal centers.²² However, trifluoroacetate may be different from triflate in nature.



Experimental Section

Materials and Measurements. Silver(I) trifluoroacetate was purchased from Aldrich and used without further purification. 3,3'-Oxybispyridine and 3,3'-thiobispyridine were prepared according to the literature procedures.¹⁹ Elemental microanalyses (C, H, N) were performed at the Advanced Analysis Center at KIST using a Perkin-Elmer 2400 CHNS Analyzer. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu K α . Thermal analyses (TGA and DSC) were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Stanton Red Croft TG 100. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr

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pellets.

Preparation of [Ag(CF₃CO₂)(3,3'-Py₂O)]. A methanol solution (6 mL) of 3,3'-Py₂O (52 mg, 0.3 mmol) was slowly diffused into an aqueous solution (6 mL) of AgCF₃CO₂ (66 mg, 0.3 mmol). Colorless crystals of [Ag(CF₃CO₂)(3,3'-Py₂O)] were obtained in 6 days in 73% yield. Mp. 195 °C (dec.). Anal. Calcd for C₁₂H₈N₂O₃F₃Ag: C, 36.67; H, 2.05; N, 7.13. Found: C, 36.40; H, 2.04; N, 7.06. IR (KBr, cm⁻¹): 1680 (s), 1208 (s); 1680.0 (s), 1572.0 (m), 1476.0 (m), 1428.0 (m), 1264.0 (m), 1208.0 (s), 1132.0 (m), 1024.0 (w), 872.0 (w), 836.0 (m), 804.0 (m), 724.0 (m), 706.0 (m).

Preparation of [Ag(CF₃CO₂)(3,3'-Py₂S)]. An ethanol solution (6 mL) of 3,3'-Py₂S (56 mg, 0.3 mmol) was slowly diffused into an aqueous solution (6 mL) of AgCF₃CO₂ (66 mg, 0.3 mmol). Colorless crystals of [Ag(CF₃CO₂)(3,3'-Py₂S)] suitable for crystallographic characterization formed at the interface, and were obtained in 6 days in 76% yield. Mp: 193 °C (dec.). Anal. Calcd for C₁₂H₈N₂O₂SF₃Ag: C, 35.22; H, 1.97; N, 6.85. Found: C, 34.90; H, 1.93; N, 6.78. IR (KBr, cm⁻¹): 1678 (s), 1572 (w), 1466 (w), 1420 (w), 1410 (m), 1322 (w), 1210 (s), 1178 (m), 1128 (s), 1020 (m), 838 (m), 802 (m), 724 (m), 704 (m).

Anion Exchange. A typical anion exchange procedure was described in our previous results.^{23,24} The exchange procedures were monitored by characteristic IR bands. The exchanged species still give sharp X-ray powder diffraction patterns and satisfactory elemental analyses.

X-ray Crystallography. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The data were corrected for Lorentz

and polarization effects. Absorption effects were corrected by the empirical ψ -scan method. The structures were solved by the Patterson method (SHELXS 97) and refined by full-matrix least square techniques (SHELXL 97).²⁵ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-194944 and CCDC-194945). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

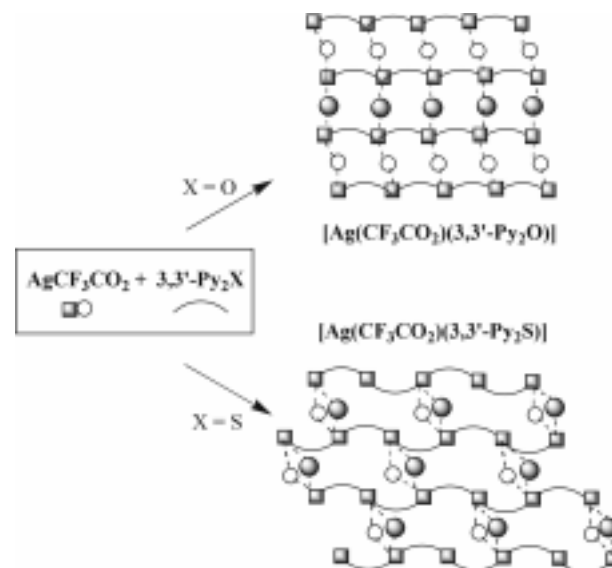
Synthesis. The reaction of AgCF₃CO₂ with 3,3'-Py₂X in appropriate solvents affords [Ag(CF₃CO₂)(3,3'-Py₂X)] (X = O, S) as shown in Scheme 1. Elemental analyses confirm that both products are 1 : 1 (Ag : Py₂X) adducts. Their basic molecular skeletons are very similar single strands, but their anions are differently bridged to give subtly different infinite structures. The reaction is independent of the mild variation of the mole ratio, the concentrations, and the solvents, indicating that the products are favorable species. The compounds are stable colorless crystals that are insoluble in water and common organic solvents, and are stable even for a week at aqueous suspensions.

Crystal Structures. The crystallographic asymmetric unit and extended structure of [Ag(CF₃CO₂)(3,3'-Py₂O)] are shown in Figure 1, and selected bond lengths and angles are listed in Table 2. There are two independent silver units in the asymmetric region of the monoclinic unit cell. The 3,3'-

Table 1. X-ray Crystal Data and Details of Data Collections and Structure Refinements

	[Ag(CF ₃ CO ₂)(3,3'-Py ₂ O)]	[Ag(CF ₃ CO ₂)(3,3'-Py ₂ S)]
Formula	C ₂₄ H ₁₆ N ₄ O ₆ F ₆ Ag ₂	C ₁₂ H ₈ N ₂ O ₂ SF ₃ Ag
Formula weight	786.15	466.13
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.383(1)	8.331(2)
<i>b</i> (Å)	19.801(3)	14.010(2)
<i>c</i> (Å)	9.297(3)	11.926(3)
β (°)	100.26(2)	95.70(2)
<i>V</i> (Å ³)	1337.4(5)	1385.1(6)
<i>Z</i>	2	4
<i>D</i> _{cal} (gcm ⁻³)	1.952	1.962
μ , mm ⁻¹	1.554	1.644
Goodness-of-fit on <i>F</i> ²	1.120	1.154
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0386	0.0589
	w <i>R</i> 2 = 0.0958	0.1541

$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. $wR2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}$ ^{1/2}, where $w = 1/\{\sigma^2 F_o^2 + (aP)^2 + bP\}$. where $P = \{\text{Max}(F_o^2, o) + 2F_c^2\}/3$.



Scheme 1

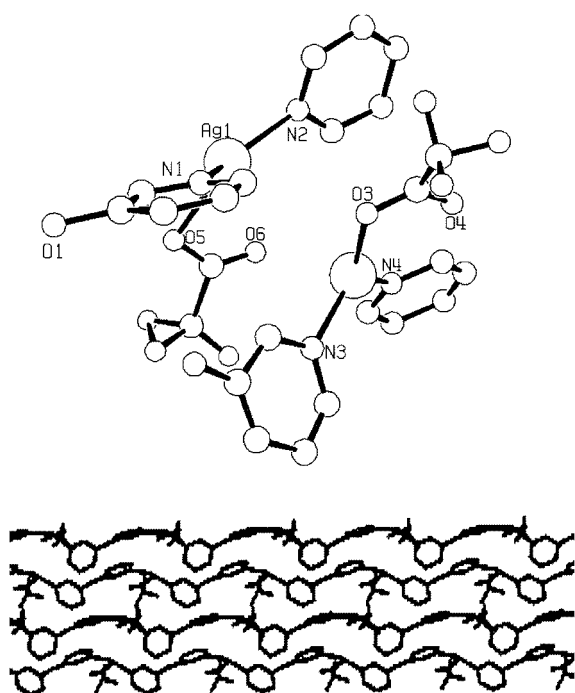


Figure 1. Unit view (top) and infinite structure (bottom) of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$. Hydrogen atoms are omitted for clarity.

Py_2O spacer connects two silver(I) ions to give a single strand ($\text{Ag-N} = 2.20(1)\text{-}2.28(1)$ Å; $\text{N-Ag-N} = 127.7(5)\text{-}131.1(5)^\circ$). The two oxygen donors of a trifluoroacetate anion even-bridge the single strands in an “up and down” mode ($\text{Ag}(1)\text{-O}(5) = 2.35(1)$ Å; $\text{Ag}(2)\text{-O}(6) = 2.70(1)$ Å; $\text{Ag}(2)\text{-O}(3) = 2.41(1)$ Å; $\text{Ag}(1)\text{-O}(4) = 2.67(1)$ Å) to give infinite molecular grids. The Ag-O bond distances are comparable to the corresponding bond in $[\text{Ag}_3(\text{NO}_3)_3(\text{Py}_2\text{S})_2 \cdot 2\text{H}_2\text{O}]$.¹⁴ Thus, the local geometry around the Ag(I) ion approximates four-coordinate arrangement.

The asymmetric unit and infinite structures of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ are shown in Figure 2, and selected bond lengths and angles are listed in Table 2. Each 3,3'- Py_2S ligand links two silver(I) ions to give a single strand. The

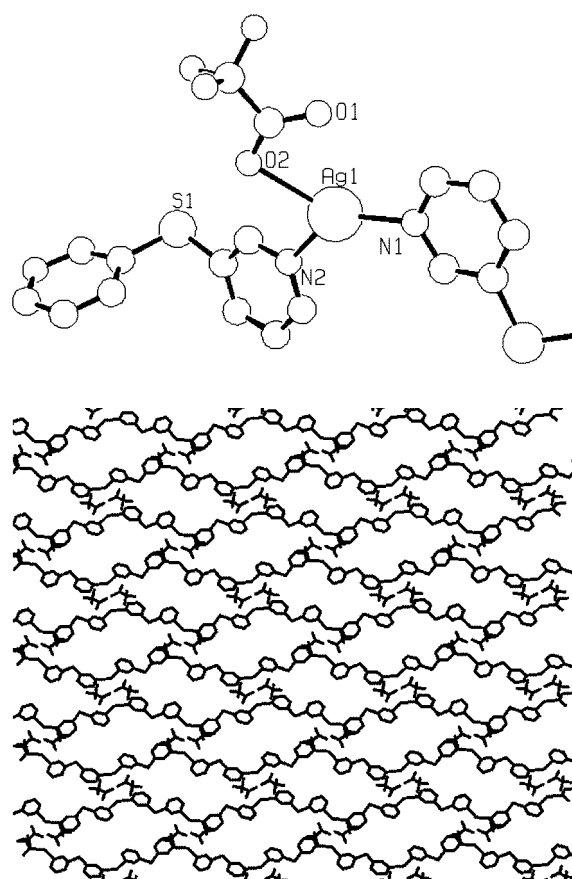


Figure 2. Unit view (top) and infinite space-filling (bottom) of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$. Hydrogen atoms are omitted for clarity.

Ag-N bonds ($2.235(5)$ Å and $2.252(5)$ Å) and the $\text{N}(1)\text{-Ag-N}(2)$ angle ($135.9(2)^\circ$) are not exceptional. The single strands are alternately double-bridged *via* the trifluoroacetate anions to give an ideal chicken-wire structure. The distances of Ag-O (CF_3CO_2^-) are $2.551(6)$ Å and $2.675(6)$ Å. The double-bridge *via* two acetate moieties induces the short interstrand Ag...Ag distance ($4.107(5)$ Å). Thus, the local geometry around the Ag(I) is a distorted tetrahedral arrangement. The Py-S-Py angle ($102.9(2)^\circ$) is much smaller than the corresponding angle Py-O-Py ($122(1)^\circ$ and $116.0(1)^\circ$) of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$.

Thermal Analyses. The thermal analyses have been used to establish a relationship between structure and properties.^{13,26} The traces of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$ and $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ show similar patterns, indicating that their skeletal structures are similar in the solid state. They are stable up to approximately 200°C in the solid state (Figure 3). Both compounds show a weight-loss corresponding to the linker and the anion was observed in the temperature range. In particular, $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ collapses more drastically than $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$, presumably due to the more weak $\text{CF}_3\text{CO}_2 \cdots \text{Ag}$ interactions.

Construction of Each Molecular Grid. 3,3'- Py_2O and 3,3'- Py_2S are similar noninnocent spacers that possess stable

Table 2. Selected Bond Lengths (Å) and Bond Angles ($^\circ$)

$[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$		$[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$	
Ag(1)-N(1)	2.28(1)	Ag(1)-N(1)	2.235(5)
Ag(1)-N(2)	2.20(1)	Ag(1)-N(2)	2.252(5)
Ag(2)-N(3)	2.27(1)	Ag(1)-O(2)	2.551(6)
Ag(2)-N(4)	2.25(1)		
Ag(1)-O(5)	2.35(1)		
Ag(2)-O(3)	2.41(1)		
N(2)-Ag(1)-N(1)	131.1(5)	N(2)-Ag(1)-N(1)	135.9(2)
N(2)-Ag(1)-O(5)	133.1(5)	N(1)-Ag(1)-O(2)	132.5(2)
N(1)-Ag(1)-O(5)	92.6(5)	N(2)-Ag(1)-O(2)	88.6(2)
N(4)-Ag(2)-N(3)	127.7(5)	C(4)-S(1)-C(9)	102.9(2)
N(4)-Ag(2)-O(3)	137.4(5)		
N(3)-Ag(2)-O(3)	90.3(4)		
C(1)-N(1)-C(5)	119(1)		
C(6)-N(2)-C(10)	116(1)		

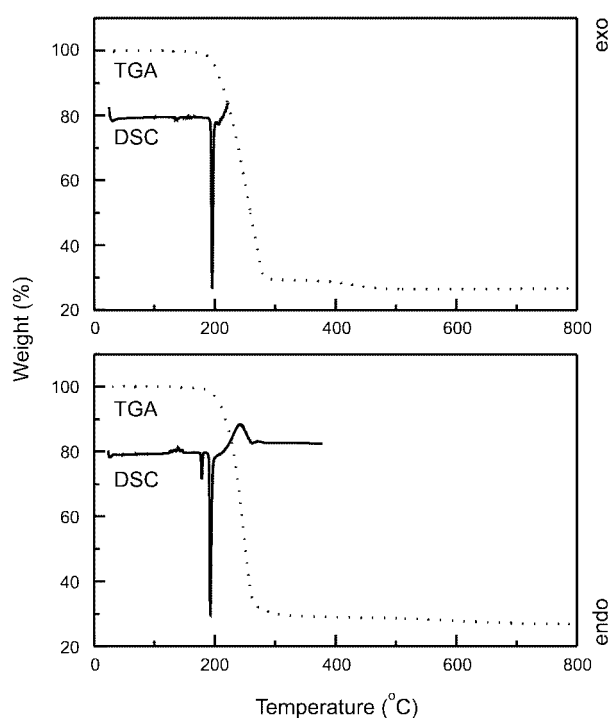


Figure 3. Overlay of TGA (···) and DSC (–) traces of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$ (top) and $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ (bottom), each recorded at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

skewed conformers with nonrigid interannular dihedral angles between two pyridyl groups.^{27,28} As expected, the reactions of AgCF_3CO_2 with the spacers basically afford the similar single strands. A striking feature is that the single strands are significantly bridged *via* the trifluoroacetate anions to give unique 2D grids in contrast to our previous triflate analogs.²⁹ That is, the induction of the 2D structures may be ascribed to the moderately coordinating ability of the trifluoroacetate anion. Our recent results have elucidated that the coordinating ability of CF_3CO_2^- anion is slightly stronger than that of CF_3SO_3^- .³⁰ The difference in coordinating ability between CF_3CO_2^- and CF_3SO_3^- is a key factor for the determination of structural dimensions. Furthermore, such non-spherical and bulky coordinating anions in contrast to symmetrical anions hampers the construction of ordered helical molecules.^{16,17}

On the other hand, there is a delicate difference between the two 2D patterns as shown in Scheme 1: “even-bridge” vs “double-bridge”. The intrinsic properties of spacers seem to trigger the delicate difference of the “noncovalent anion-bridge”. There are actual differences between the two spacers in the size, the bond angle, the lone-pair delocalization of chalcogens, the conformational energy barrier, and the donating ability of nitrogen atoms.^{17,27,28} Thus, for the present structures, the C-S-C angle of 3,3'-Py₂S is smaller than the corresponding value of 3,3'-Py₂O. The difference in donating ability between the spacer ligands exists in the structures.

For both compounds, the $\text{CF}_3\text{CO}_2 \cdots \text{Ag}$ interactions are not strong, but are slightly different in the solid state. In order to verify the weak interactions, a typical anion

exchange was attempted in a typical aqueous media. A preliminary anion exchange indicates that the CF_3CO_2^- anions are exchanged by ClO_4^- or PF_6^- anions. We expected that the anion of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ could be more easily exchanged due to the longer anion \cdots silver distance. However, the anion exchange of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{S})]$ is slower than that of $[\text{Ag}(\text{CF}_3\text{CO}_2)(3,3'\text{-Py}_2\text{O})]$, indicating that the anion exchangeability is governed by the nature of the spacer rather than the distance of $\text{Ag}(\text{I}) \cdots \text{CF}_3\text{CO}_2^-$. The hydrophilicity of a spacer may be an important factor in the anion exchange.

In conclusion, the present results show that the moderate coordinating anions are connectors for higher dimensions. Thus, the coordinating ability and shape of anions should be cautiously considered in the construction of molecular buildings. A direct comparison between 3,3'-Py₂S and 3,3'-Py₂O on the same anions represents an important conceptual advance: delicate difference of spacer results in delicate difference of product. In particular, simple anion exchange may be useful in the generation of new species. More systematic studies including related spacer ligands are in progress for more effective rational control that may contribute to the development of useful high dimensional molecular materials.

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