Ligand-Rearrangement-Induced Transformation from a 3D Supramolecular Network to a Discrete Octanuclear Cluster: A Good Detector for Pb$^{2+}$ and Cr$_2$O$_7^{2-}$

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Supporting Information

ABSTRACT: A three-dimensional supramolecular framework containing both left- and right-handed helices, \([\{\text{Zn}(\text{TTPA})\text{Cl}_2\}\cdot 1.63\text{H}_2\text{O}\}]_n \) (1), has been converted to a novel octanuclear cluster containing a metal–organic framework, \([\text{Zn}_8(\text{ptptp})_6\text{Cl}_2]\text{(ClO}_4\text{)}_2\cdot 4\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O} \) (1b), induced by ligand rearrangement during a solvothermal process. The luminescent properties of 1b indicate that the material can act as a selective probe toward Pb$^{2+}$ and Cr$_2$O$_7^{2-}$.

INTRODUCTION

Metal–organic frameworks (MOFs) are becoming a well-known subset of materials science and chemical research. The main features of MOFs that make them so highly studied are their tailored properties resulting from their regular structures and high crystallinity. These properties make MOFs well suited for the fields of gas storage and separation, sensing, and catalysis, and along with biomimetic applications. One particular MOF phenomenon, single-crystal to single-crystal (SC–SC) transformations, is becoming increasingly well studied as it allows for the ability to incorporate the functional groups and metal centers into crystallographically exact locations within the MOF, allowing the resulting structure to achieve properties that are often difficult to induce in a MOF solvothermally. Typically, the mild conditions of SC–SC transformations do not alter the structure of the MOF; however, rearrangements in the coordination environments of metal ions and ligands have been observed. Additionally, the SC–SC transformation allows for the crystallographic structural determination of chemical species that are often difficult to be produced in solution phase. Because of this, the SC–SC transformation allows for the generation of novel coordination assemblies with unique reactivities, something that can be of great use in areas such as catalysis or separations. In particular, SC–SC transformations are ideally suited for the generation of novel multimetallic assemblies, as solvothermal syntheses containing multiple metal species typically result in a mixture of multiple phases, or could potentially require cumbersome multistep pathways. In this work, we chose a known ligand, TTPA, and investigated its three-dimensional (3D) supramolecular framework, \([\{\text{Zn}(\text{TTPA})\text{Cl}_2\}\cdot 1.63\text{H}_2\text{O}\}]_n \) (1) (TTPA = tris(4-(1H-1,2,4-triazol-1-yl)phenyl)amine). The 3D network is interesting because it has both left- and right-handed helices. Structure 1 contains only water as the lattice guests, which suggested the possibility that \(\text{H}_2\text{O}\) could be replaced by other solvents. The irreversible and distinct SC–SC transformation triggered by solvent exchange afforded \([\{\text{Zn}(\text{TTPA})\text{Cl}_2\}\cdot 0.5\text{CH}_3\text{OH}\cdot \text{H}_2\text{O}\}]_n \) (1a). More interestingly, under hydrothermal conditions, I yielded a novel discrete octanuclear \(\text{Zn}^2+ \) cluster, \([\text{Zn}_8(\text{ptptp})_6\text{Cl}_2]\text{(ClO}_4\text{)}_2\cdot 4\text{CH}_3\text{OH}\cdot 2\text{H}_2\text{O} \) (ptptp = 2-(5-(6-(5-(pyridin-2-yl)-4H-1,2,4-triazol-3-yl)pyridin-2-yl)-4H-1,2,4-triazol-3-yl)-pyridine) (1b), through an in situ reaction and unusual
geometric arrangement. In fact, this result is the first example of switching the dimensionality of a framework via an in situ reaction triggering ligand rearrangement. Investigation into its luminescent properties indicates that 1b represents the first example of a triazole-based material with selective recognition toward Pb\(^{2+}\) and Cr\(^{2+}\).

### RESULTS AND DISCUSSION

**Structure Description.** Supramolecular complex 1 crystallized in the monoclinic space group P2\(_1\)/n (Table 1). Within the asymmetric unit of 1, one Zn\(^{2+}\) ion, one TTPA ligand, and two Cl\(^{-}\) anions were observed (Figure 1a). The Zn\(^{2+}\) ion adopts a distorted tetrahedral coordination geometry, which is defined by two Cl\(^{-}\) anions alongside two N\(_{\text{triazole}}\) atoms. The Zn–Cl bond distances fall within the 2.2250(7) to 2.2413(7) Å range, and the variance within the Zn–N distances are from 2.012(2) to 2.019(2) Å. All of the bond distances are within the normal range for zinc complexes.\(^{11}\) The alternating connectivity of the Zn\(^{2+}\) ions and the TTPA ligands gives rise to an infinite one-dimensional (1D) chain expanding along the b axis. The formation of helixes is due to the flexibility between the triazole and benzene rings in TTPA. The dihedral angles of the three triazole rings compared to their neighboring benzene rings are 2.2°, 18.4°, and 21.9°. The Zn\(^{2+}\) ions are linked by two of the triazole groups on TTPA, forming a 1D Zn–TTPA helical chain, whose pitch is 24.401(10) Å (Figure 1b). In the crystal structure, chains with the same chirality stack by the a axis, while along the c axis, the chains alternate chirality. This chain altering structure forms a porous 3D supramolecular framework with free-water molecules sitting in the cavities (Figure 1d).

Inspired by studies on SC–SC transformations,\(^{12}\) 1 was immersed in CH\(_3\)OH, yielding orange-yellow crystals of 1a. X-ray structural analysis revealed that 1a and 1 are isostructural only with the addition of a half equivalent of methanol in the asymmetric unit of 1a (Figure S1a). Similar to 1, Zn\(^{2+}\) ions are coordinated with the two N\(_{\text{triazole}}\) atoms from TTPA and two Cl\(^{-}\) ions; however, the Zn–N bond distances instead ranged from 2.016(3) to 2.020(3) Å while the Zn–Cl bonds ranged from 2.2336(12) to 2.2516(13) Å. For the µ\(_2\)-bridged TTPA ligand in 1a, the dihedral angle between the benzene and triazole rings are 5.5° and 19.4° in the helical chains and 21.5° for others. The alternating linkage of Zn\(^{2+}\) and TTPA results in a slightly larger pitch of 24.401(10) Å between the chiral chains as compared to 1. We are currently interested in the effect of solvents on the topological configuration of helical networks, as they can tune geometric arrangement. In fact, this result is the first example of switching the dimensionality of a framework via an in situ reaction triggering ligand rearrangement. Investigation into its luminescent properties indicates that 1b represents the first example of a triazole-based material with selective recognition toward Pb\(^{2+}\) and Cr\(^{2+}\).

### Table 1. Crystallographic Data and Refinement Details for 1, 1a, and 1b

|       | 1       | 1a      | 1b       |
|-------|---------|---------|---------|
| formula | C\(_{24}\)H\(_{21.25}\)Cl\(_{2}\)N\(_{10}\)O\(_{1.63}\)Zn | C\(_{24}\)H\(_{21.25}\)Cl\(_{2}\)N\(_{10}\)O\(_{1.5}\)Zn | C\(_{118}\)H\(_{86}\)Cl\(_{4}\)N\(_{54}\)O\(_{14}\)Zn\(_8\) |
| M (g mol\(^{-1}\)) | 612.03 | 616.79 | 3149.16 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | P2\(_1\)/n | P2\(_1\)/n | C2/c |
| temperature | 173.00(10) | 113(2) | 173(2) |
| a (Å) | 5.44989(12) | 5.426(2) | 4.279(2) |
| b (Å) | 24.2409(6) | 24.401(10) | 13.776(6) |
| c (Å) | 20.7642(7) | 20.717(9) | 24.6543(14) |
| α (deg) | 90 | 90 | 90 |
| β (deg) | 96.743(2) | 96.472(9) | 123.1690(10) |
| γ (deg) | 90 | 90 | 90 |
| V (Å\(^3\)) | 2724.18(13) | 2726(2) | 12167.9(11) |
| Z | 4 | 4 | 4 |
| F (000) | 1249.0 | 1260 | 6368 |
| ρ\(_{\text{emp}}\) (mg m\(^{-3}\)) | 1.492 | 1.503 | 1.719 |
| μ (mm\(^{-1}\)) | 3.401 | 1.138 | 1.726 |
| data/restraints/params | 4856/18/388 | 4817/30/379 | 10721/52/921 |
| GOF on F\(^2\) | 1.137 | 1.110 | 1.048 |
| R\(_{1}\) (I = 2σ(I)) | 0.0391 | 0.0501 | 0.0751 |
| wR\(_{2}\) (all data) | 0.1190 | 0.1510 | 0.2228 |

\(^{1a}R_1 = \sum |F_o| - |F_c|)/|F_o|; \(^{1b}wR_2 = \sum \omega w/(|F_o|^2 - |F_c|^2)/w)^2 |1/2.\)
the dihedral angle between the aromatic rings and the pitch of the self-assembled helical spring. The central projection of the 3D supramolecular structure (Figure S1b) shows that the methanol and water molecules lie in the voids between the neighboring chains.

It is interesting to note that when 1, NaClO₄·H₂O, and CH₃OH were added into a 25 mL Te octanuclear ZnII moieties can be deduced from the in situ generation of the ligand ptptp. To the best of our knowledge, 1b is the first observed example of this type of in situ ligand generation from TTPA to ptptp. Single-crystal X-ray analysis indicated that 1b crystallizes in the monoclinic space group and the C2/c crystal system. The asymmetric unit is composed of four Zn⁴⁺ ions, three ptptp ligands, one Cl⁻ anion, one ClO₄⁻ anion, two methanol molecules, and one water molecule. It was observed that there are in fact two different Zn⁴⁺ coordination modes in 1b. Zn2 is situated in a distorted octahedral coordination environment ligated by six N atoms from three distinct ptptp ligands while Zn1, Zn3, and Zn4 exhibited a distorted square pyramidal geometry. Their geometry consists of four N_{ptptp} atoms and one μ₃-Cl atom (Figure 2a). All Zn–N bonds range from 2.173(5) to 2.515(5) Å, with the Zn–Cl bonds ranging from 2.3974(18) to 2.3974(18) Å, both of which are longer than those of 1a and 1b.

Figure 2. (a) Coordination modes of Zn atoms in 1b. (b) Coordination mode of the ptptp ligand. (c) {Zn₈(ptptp)₆Cl₂} cluster and Zn⁴⁺ metal skeleton for the bicapped trigonal antiprism cluster. (symmetry code: A −x, y, 0.5 − z.) (d) Fundamental structural unit of the {Zn₈(ptptp)₆Cl₂} cluster. (e) Stacking of the {Zn₈(ptptp)₆Cl₂} clusters in 1b. Purple, Zn; blue, N; green, Cl; white, C; gray, H.

Ptptp is a hepta-dentate ligand which ligated the three Zn atoms, forming an isolated fanlike {Zn₈(ptptp)₆Cl₂} cluster (Figure 2b). An octanuclear cluster building unit has been previously observed in the Mn⁷⁺ and Cd⁶⁺ analogues. The octanuclear Zn⁴⁺ moiety can be defined as a bicapped trigonal antiprism polyhedron, as shown in Figure 2c. The Zn1, Zn3, and Zn4 atoms are connected by μ₃-Cl in an approximately planar triangular geometry. The triangles of Zn1–Zn3–Zn4 and Zn1A–Zn3A–Zn4A serve as the top and bottom planes of the antiprism with the remaining Zn2 and Zn2A being the up and down of the triangular faces, respectively. The adjacent Zn atoms are linked through the triazole rings of the ptptp ligands in the manner of Zn1–N–N–Zn4A, Zn4–N–N–Zn1A, Zn3–N–N–Zn3A, and Zn(1/3/4)–N–N–Zn2. The distance between the two Zn atoms in two triangular planes is 4.47 Å with the mean distance between the cap Zn and the neighbor in the triangular plane is 4.63 Å. The dihedral angles between the pyridine rings and the triazole rings are in the range of 1.9–38.5°. Each Zn atom coordinates with three ptptp ligands and the whole {Zn₈(ptptp)₆Cl₂} clusters is surrounded by six ptptp ligands, as indicated in Figure 2d. The stacking of the {Zn₈(ptptp)₆Cl₂} clusters gives rise to the final structure (Figure 2e), with ClO₄⁻, methanol, and water molecules being dispersed throughout the {Zn₈(ptptp)₆Cl₂} clusters, balancing the electrical charges and stabilizing 1b.

**Luminescence Properties.** Hexavalent chromium Cr(VI) is extensively utilized in industrial applications such as paint production, leather tanning, and steel manufacturing, which has resulted in extensive amounts of Cr(VI) environmental pollution. In particular, the U.S. Environment Protection Agency (EPA) considers Cr₂O₇²⁻ as a group “A” human carcinogen for its mutagenicity, carcinogenicity, and teratogenicity in the human body. Another known environmental contaminant, lead(II), is also known to have severe effects on the environment as well as human health. Lead accumulation within the body can lead to reproductive, neurological, cardiovascular, and developmental disorders. Currently, atomic absorption spectrometry and inductively coupled plasma mass spectrometry are used for detecting lead(II) ions, but they typically require complex procedures or equipment which makes them unsuitable for on-site analyses. Fluorescent detection is gradually becoming a promising Cr₂O₇²⁻ and Pb²⁺ detection strategy because of its operational simplicity, minimal cost, on-site monitoring capabilities, and high selectivity. Therefore, fluorescent probes for the selective determination of Cr₂O₇²⁻ and Pb²⁺ concentrations are highly sought after.

As shown in Figure 3a, TTPA is luminescent in dimethylformamide (DMF) at ambient temperatures, exhibiting a broad emission maximum at λ_{em,max} = 320 nm. A red shift occurs to compounds 1a and 1b compared with TTPA. The exhibited red-shifted results in relatively strong green and yellow fluorescent emission bands at λ = 597 and 525 nm, respectively (Figure 3b). The major emission bands of TTPA and 1a show a similar band shape. The band shape of the two components can neither be classified as neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer. The most likely result is the intraligand fluorescent emission, something which is also observed for the free TTPA ligand in DMF. In comparison with the free ligand fluorescent emissions and 1a in solution, 1b is both narrow and red-shifted. The aromatic rings of TTPA within 1b lead to the chromophores, with the observed emission due to the π → π* transition.

Complex 1b was soaked in aqueous solutions containing different anions (F⁻, Cl⁻, Br⁻, I⁻, SO₄²⁻, ClO₄⁻, CO₃²⁻, BF₄⁻, NO₃⁻, Cr₂O₇²⁻, NO₂⁻, and OAc⁻). The luminescent measurements show that the different anions greatly affect the luminescent intensity of 1b. Remarkably, Cr₂O₇²⁻ has the largest quenching effect of the studied anions (Figure 4a). Although several reports on MOF-based anion exchange have been reported, there are few examples on the capture of pollutant anions with luminescent Zn⁴⁺ complexes. This unique feature resulted in further studies on the capture capacity of 1b toward Cr₂O₇²⁻.
At room temperature, 0.01 mmol 1b was placed into an aqueous solution containing 0.005 mmol of K2Cr2O7 and the mixture was stirred continuously. The solution was evaluated by taking liquid UV/vis spectroscopic analysis at certain intervals. The absorption intensity of the main band of Cr2O7^{2−}, around 𝜆 = 333 nm, showed a distinct decrease over time, thus demonstrating that Cr2O7^{2−} ions were gradually included into the channels of 1b. By soaking 1b for 12 h in a solution of K2Cr2O7, the UV/vis absorption intensity of the Cr2O7^{2−} ions remained almost unchanged, corresponding to a concentration decrease of about 29.7% (Figure 4b). The luminescent intensity of 1b gradually decreased during the guest incorporation process, which corresponded to the quenching effect of Cr2O7^{2−} (Figure 4c).

Upon adding 1–3 equiv of Pb^{2+} (1 × 10^{-3}, 2 × 10^{-3}, and 3 × 10^{-3} M), the emission intensity of 1b increases significantly with respect to 1b. The peak at 525 nm is about four times as intense as the corresponding band in the absence of Pb^{2+}. The same experiments were performed with Ni^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+}, and Ca^{2+} ions to clarify the Pb^{2+} results. The emission intensity gradually decreased in the presence of 1–3 equiv of these ions, except for Ni^{2+}, the emission intensity of which stayed mostly unchanged (Figure 5). To the best of our knowledge, this is the first report of a triazole-based octanuclear cluster being used as a selective luminescent probe for Pb^{2+} and Cr2O7^{2−}.

**CONCLUSIONS**

A porous 3D supramolecular framework containing right- and left-hand helixes has transformed into an octanuclear cluster through a ligand rearrangement induced by solvothermal conditions. The resulting octanuclear ZnII complex has been demonstrated as a selective sensor toward Pb^{2+} and Cr2O7^{2−}.

**EXPERIMENTAL SECTION**

General Remarks. All the reagents were commercially available and used without further purification. The elemental analysis of carbon, nitrogen, and hydrogen was performed on a PerkinElmer 240 elemental analyzer. The photoluminescence spectra were recorded by an MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source. The powder sample was soaked in aqueous solutions containing various anions (F−, Cl−, Br−, I−, NO2−, ClO4−, SO4^{2−}, CO3^{2−}, BF4−, NO3−, and OAc−), giving the resultant turbid liquid for direct luminescence measurement.

**Synthesis of ([Zn(TTPA)Cl2]·1.63H2O)n (1).** A mixture of TTPA (0.0447 g, 0.1 mmol) and ZnCl2 (0.0409 g, 0.3 mmol) was dissolved in C2H5OH (8 mL) and H2O (2 mL). The final mixture was placed in a 25 mL Teflon vessel and sealed under autogenous pressure while being heated at 120 °C for 3 days. The autoclave was then cooled to room temperature after 12 h. Light-yellow rod-shaped crystals of 1 were obtained, dried in air,
and collected in 30% yield (based on TTPA). Elemental analysis: calcd for C_{24}H_{21.25}Cl_2N_{10}O_{1.63}Zn (%): C, 47.09; H, 3.50; N, 22.88. Found: C, 46.88; H, 3.32; N, 22.94.

**Synthesis of [[Zn(TTPA)Cl_2]·0.5CH_3OH·H_2O]_n (1a).** Proper sized crystals (100 mg) of 1 were soaked in 10 mL of CH_3OH for 12 h. Orange-yellow crystals suitable for single-crystal X-ray diffraction were separated and washed thoroughly with CH_3OH and then dried in air. Yield: 30%. Elemental analysis: calcd (%) for C_{24.5}H_{22}Cl_2N_{10}O_{1.5}Zn: C, 47.71; H, 3.60; N, 22.71; found: C, 47.76; H, 3.65; N, 22.63.

**Synthesis of [Zn_8(ptptp)_6Cl_2](ClO_4)_2·4CH_3OH·2H_2O (ptptp = 2-(5-(6-(5-(Pyridin-2-yl)-4H-1,2,4-triazol-3-yl)-pyridin-2-yl)-4H-1,2,4-triazol-3-yl)pyridine) (1b).** A mixture of 1 (100 mg) and NaClO_4 (1 g) was dissolved in H_2O (2 mL) and CH_3OH (10 mL). The mixture was then placed in a 25 mL Teflon vessel and sealed under autogenous pressure before being heated at 150 °C for 3 days. The autoclave was then cooled to room temperature for 15 h. Yellow rod-shaped crystals of 1b were obtained, dried in air, and collected in 40% yield (based on 1). Elemental analysis: calcd for C_{59}H_{43}Cl_2N_{27}O_{7}Zn_4 (%): C, 45.00; H, 2.75; N, 24.02. Found: C, 45.08; H, 2.72; N, 23.94.

**Figure 5.** Emission spectra of complex 1b at room temperature in dimethyl sulfoxide (10^{-3} M), which was excited at 315 nm in the presence of 0–3 equiv of Pb^{2+} (top left), Ni^{2+} (top right), Mg^{2+} (middle left), and Cd^{2+} (middle right), Zn^{2+} (bottom left), and Ca^{2+} (bottom right). Black line, no addition; red line, 1 equiv; green line, 2 equiv; blue line, 3 equiv.

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**Notes**
The authors declare no competing financial interest.

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**ASSOCIATED CONTENT**

# Supporting Information
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Bond lengths and angles for 1, 1a, and 1b; ellipsoid view of the asymmetric unit; PXRD after soaking experiment; scanning electron microscopy images of 1b; and luminescent properties (PDF), CCDC no. 1811250 for 1 (CIF), CCDC no. 1811978 for 1a (CIF), CCDC no. 1058049 for 1b (CIF).
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