

The Covalent and Coordination Co-Driven Assembly of Supramolecular Octahedral Cages with Controllable Degree of Distortion

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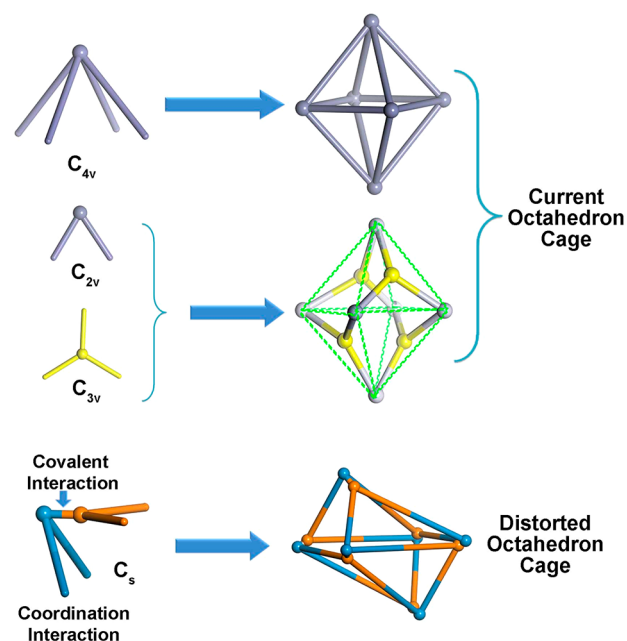
Supporting Information

ABSTRACT: Discovering and constructing novel and fancy structures is the goal of many supramolecular chemists. In this work, we propose an assembly strategy based on the synergistic effect of coordination and covalent interactions to construct a set of octahedral supramolecular cages and adjust their degree of distortion. Our strategy innovatively utilizes the addition of sulfur atoms of a metal sulfide synthon, $[\text{Et}_4\text{N}][\text{Tp}^*\text{WS}_3]$ (A), to an alkynyl group of a pyridine-containing linker, resulting in a novel vertex with low symmetry, and of Cu(I) ions. By adjusting the length of the linker and the position of the reactive alkynyl group, the control of the deformation degree of the octahedral cages can be realized. These supramolecular cages exhibit enhanced third-order nonlinear optical (NLO) responses. The results offer a powerful strategy to construct novel distorted cage structures as well as control the degree of distortion of supramolecular geometries.

Supramolecular assembly provides a powerful route to construct diverse metal-containing entities with designed geometries and symmetries, owing to the highly directional and predictable nature of the metal–ligand coordination.¹ Supramolecular cages² featuring predesigned polyhedron geometries, windows, and cavities have captured widespread attention in areas as diverse as chemical sensing,³ catalysis,⁴ molecular encapsulation,⁵ and separations.⁶ Major developments have taken place in the assembly of supramolecular cages by coordination of Lewis-basic donor subunits to Lewis-acidic acceptor subunits.⁷ The usually high predictability of the interligand angles around the metal center enables the design of supramolecular cages, although the limited number of possibilities hampers further structural diversity in their design.⁸ Combining the diversity of angles offered by coordination and covalent bonds⁹ appears a promising strategy for constructing unique supramolecular cage architectures.¹⁰ In recent years, covalent bonds have been used to build molecular cages, however, their vertices are still based on the single coordination or covalent interaction.¹¹ Employing both coordination and covalent interactions to construct supramolecular cages with novel vertices represents an exciting challenge.

To date, the kinds of vertices based on coordination interactions in supramolecular nanocage architectures are limited.¹² The nature of the ligand field leads to a high symmetry around the metal center forming the vertices of the supramolecular cages, which makes increasing structural diversity and access to systematically distorted cage structures challenging.¹³ For example, most of the reported octahedral supramolecular cages are based on specific vertices, and their high local symmetry (C_{2v} , C_{4v} , and C_{3v}) leads to highly symmetric octahedral supramolecular cages (Scheme 1).¹⁴ As

Scheme 1. Construction of the Existing Octahedron Cages and of Distorted Octahedron Cages by a New Strategy Reported Here



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illustrated in Scheme 1, a vertex that contains coordination and covalent interactions would possess a lower symmetry (C_s), thus providing an opportunity to construct the distorted octahedron-type cages.

On the basis of above considerations, we present a strategy to construct distorted octahedron-type cages and achieve the adjustment of their distortion by employing synergistic effects between coordination and covalent interactions. The precursor $[\text{Et}_4\text{N}][\text{Tp}^*\text{WS}_3]$ (Tp^* = hydridotris(3,5-dimethylpyrazol-1-yl)borate) (**A**) (Figure 1a) was used as the cage vertex because

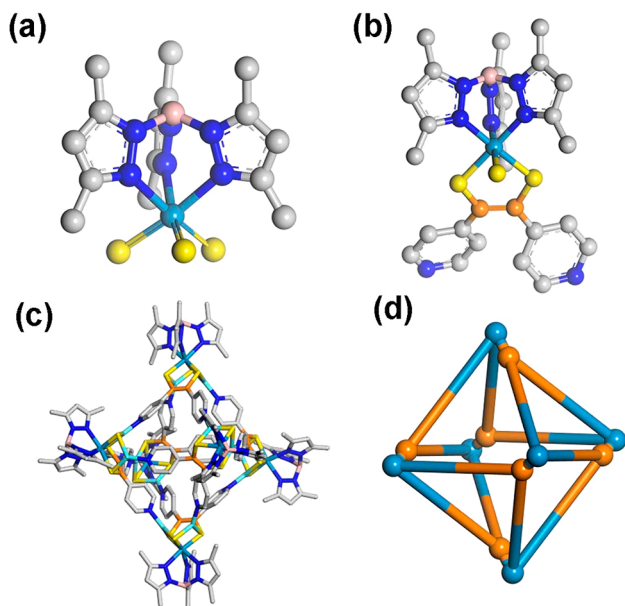


Figure 1. (a) The structure of **A**. (b) The proposed structure of intermediate **INT-1**. (c) The structure of cage **1**. (d) The topology of cage **1**. The cyan balls and orange balls respectively stand for the Tp^*WS_3 unit and reacted alkynyl ligand unit in Figure 1d. Color codes: The C atoms with an orange color represent the C atoms on the newly generated $\text{C}=\text{C}$ bonds derived from the addition reaction between the S atoms and the alkynyl groups. W (cyan), Cu (azure), S (yellow), N (blue), C (silver), B (pink). The hydrogen atoms, guest solvent, and OTf anions were omitted for clarity.

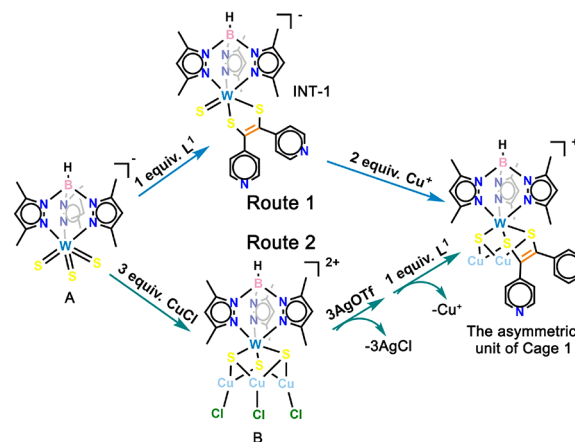
the donor sulfur atoms can react with linear alkynyl linkers¹⁵ to generate covalent attachment of a functional linker that is subsequently reacted with Cu(I) ions, leading to the emergence of variable angular orientations. This strategy provides the first family of octahedral cages where different degrees of distortion can be fine-tuned. This relies on adjusting the length of the alkyne ligand and the position of the alkynyl function. Furthermore, the assembly process from **A** to the supramolecular cage structures significantly enhances their third-order nonlinear optical (NLO) responses.

In the W(VI) synthon $[\text{Et}_4\text{N}][\text{Tp}^*\text{WS}_3]$ (**A**), which was synthesized according to the literature,¹⁶ the Tp^* ligand occupies three coordination sites of the W(VI) ion (Figure 1a), and three sulfur atoms complete the octahedral coordination environment. Two sulfur atoms of Tp^*WS_3 can react with the triple bond of 1,2-bis(4-pyridyl)ethyne (L^1) and form two $\text{S}-\text{C}$ covalent bonds of the 1,2-enedithiolato intermediate (**INT-1**) (Figure 1b). The formation of **INT-1** was confirmed by ESI-TOF MS (Supporting Information (SI), Figure S1). This reaction lowers the local symmetry of **A**, thus leading to a vertex of C_s symmetry instead of the higher

symmetry usually encountered (C_{2v} , C_{4v} , or C_{3v}). The remaining terminal S and the two S (1,2-enedithiolato) atoms in **INT-1** are available for reaction with Cu(I) ions, which can further bind to the pyridine donor of another **INT-1** unit to generate the supramolecular cage.

Thus, the reaction of **INT-1** with 2 equiv of $[\text{Cu}(\text{MeCN})_4]\text{OTf}$ afforded a WS_3Cu_2 core-based cationic octahedral cage $[\text{Tp}^*\text{WS}_3\text{Cu}_2(\text{L}^1)_6](\text{OTf})_6$ (**[1]**)(OTf)₆ (Figure 1c) as a result of additional interactions between the Cu(I) centers and the 1,2-enedithiolato S atoms (Scheme 2, route 1). Because the

Scheme 2. Two Different Approaches Leading to the Self-Assembly of Octahedral Cage **1**



product was obtained in only 20% yield, we examined an alternative strategy consisting in the one-pot reaction between **A**, $[\text{Cu}(\text{MeCN})_4]\text{OTf}$, and L^1 (SI, section 2.4, Method 1). This self-assembly procedure led to **[1]**(OTf)₆ with improved yield of ca. 70%. Its ESI-TOF MS spectrum contains three signals at $m/z = 1917.8164$, 1401.1488 , and 1091.1168 with the correct isotope distribution patterns for an assignment to $[\text{1}](\text{OTf})_3^{3+}$, $[\text{1}](\text{OTf})_2^{4+}$ and $[\text{1}](\text{OTf})^{5+}$, respectively (SI, Figures S2–S4). Furthermore, diffusion ordered spectroscopy (DOSY) revealed that both the aromatic signals and the aliphatic signals belong to a single species, with a diffusion coefficient of $4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which confirms the high purity of the supramolecular cage **1** (SI, Figure S15).

The crystal structure of **[1]**(OTf)₆ was determined by single-crystal X-ray diffraction (SCXRD) (Figure 1c and SI, Figures S24–S27). It crystallizes in the trigonal space group $R\bar{3}$. The distorted trigonal planar geometry of each Cu(I) center in the $\text{Tp}^*\text{WS}_3\text{Cu}_2$ units is completed by a pyridyl N atom and two μ_3 -S atoms. Interestingly, the $\text{Tp}^*\text{WS}_3\text{Cu}_2$ units connect with each other through both coordination ($\text{Cu}(\text{I}) \cdots \text{pyridine}$) and covalent interactions ($\text{S}-\text{C}=\text{C}$). If we assign the Tp^*WS_3 unit and the linker as the secondary building units (SBUs), cage **1** would be simplified as an octahedral structure (Figure 1d), of lower symmetry compared with the reported octahedron cage structures. As detailed in SI, Figure S43, the values of the angle γ^1 in cage **1** are 59.51° and those of angles α^1 and β^1 are the same, 60.24° , resulting in nearly equilateral triangular faces (SI, Figure S43 and Table S2). In view of the presence of covalent interactions between the linker and the Tp^*WS_3 units, the whole $\text{Tp}^*\text{WS}_3\text{Cu}_2(\text{L}^1)_6$ cluster can be considered as the vertex of cage **1**, and it contains both the Lewis-basic donor and Lewis-acidic acceptor. To our knowledge, cage **1** is the first example of supramolecular octahedral

based on the vertex with both covalent and coordination interactions.¹⁴

The reaction of **A** with 3 equiv of CuCl produces a highly stable heterometallic cluster $[\text{Et}_4\text{N}][\text{Tp}^*\text{WS}_3(\text{CuCl})_3]$ (**B**),¹⁷ with an incomplete cubane-like core structure; each Cu(I) is in a trigonal-planar coordination environment defined by one terminal Cl and two μ_3 -S atoms (SI, Figure S28). Its reaction with AgOTf and **L**¹ afforded the same octahedral cage $[\mathbf{1}](\text{OTf})_6$ (route 2 in Scheme 2 and SI section 2.4, Method 2). The alkyne group of **L**¹ reacted with two S atoms of the $\text{Tp}^*\text{WS}_3\text{Cu}_3$ unit to give an 1,2-enedithiolate moiety by in situ formation of C–S bonds, and this triggered the elimination of one Cu(I) atom.

The unique approach described above allows us to investigate the influence of the pyridyl alkyne-containing spacer length on the structure of the resulting cage. With the longer alkynyl ligands 1,4-bis(pyridine-4-ylethynyl)benzene (**L**²) and 4,4'-bis(pyridine-4-ylethynyl)-1,1'-biphenyl (**L**³) (Scheme 3), the octahedral cage compounds $[\mathbf{2}](\text{OTf})_6$ (SI,

Scheme 3. Rigid Linear Alkynyl-Containing Ligands Allowing a Control of the Distortion of the Octahedral Cages Generated (The Cyan Balls and Orange Balls Respectively Stand for the Tp^*WS_3 Units and Reacted Alkynyl Ligand Units.)

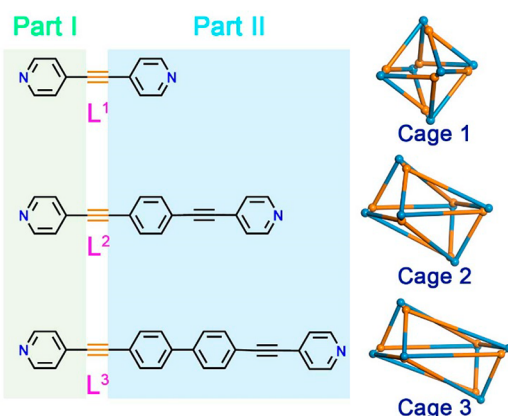


Figure S32) and $[\mathbf{3}](\text{OTf})_6$ (SI, Figure S39) were successfully prepared, respectively (SI, sections 2.5 and 2.6). Because only one alkyne group of the ligand can undergo coupling with the sulfur atoms of the Tp^*WS_3 unit, an unsymmetrical situation arises for the spacer (Scheme 3). When the length of Part I (4.30 Å) is approximately equal to that of Part II (4.26 Å), as in ligand **L**¹, a nearly regular octahedral supramolecular structure results, whereas an octahedron with an increasing degree of distortion is generated when the value of Part II increases, which impacts the angles in the vertex (SI, Figures S24, S29, and S36). Thus, the increased value of Part II (11.080 Å) in **L**² leads to a significant decrease of α while β and γ notably increase, with α^2 , β^2 and γ^2 , being 36.87°, 71.57°, and 71.57°, respectively. In cage **3**, the length of Part II in **L**³ is increased to 15.34 Å, yielding an even more distorted octahedron, with angles α^3 , β^3 , and γ^3 of 30.13°, 74.93°, and 74.93°, respectively (SI, Table S2). Consequently, by adjusting the length of one part of the ligand, it is possible to control the degree of distortion of the resulting supramolecular cages.

Among the very important third-order nonlinear optical (NLO) materials, W–S–Cu compounds show unique NLO performance and this led us to investigate the NLO properties

of **A** and cage compounds $[\mathbf{1}](\text{OTf})_6$, $[\mathbf{2}](\text{OTf})_6$, and $[\mathbf{3}](\text{OTf})_6$. By using the Z-scan technique with 15 ps width laser pulse at 532 nm, **A** showed no detectable NLO response in MeCN (SI, Figures S45 and S46). However, after self-assembly of **A** with Cu^+ ions and the alkynyl ligands, these cage compounds exhibited significant NLO responses in MeCN with reversed saturable absorption (Figure 2a, SI, Figures S53

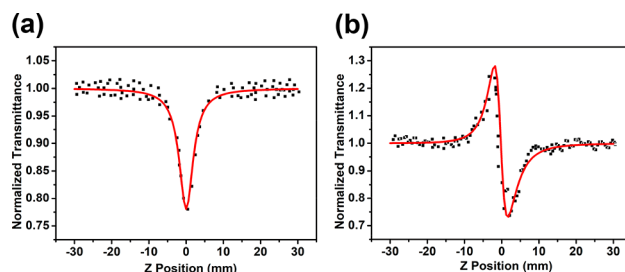


Figure 2. Third-order NLO responses for $[\mathbf{1}](\text{OTf})_6$ in MeCN obtained for 15 ps, 532 nm laser pulses. (a) Normalized Z-scan data for $[\mathbf{1}](\text{OTf})_6$ under open-aperture conditions, displaying a reversed saturable absorption. (b) Normalized Z-scan data for $[\mathbf{1}](\text{OTf})_6$ under closed aperture conditions, displaying nonlinear refraction performance. Dots represent experimental data, while the red solid lines stand for the numerical simulations.

and S55) and nonlinear refraction performance (Figure 2b, SI, Figures S54 and S56) under the same experimental conditions. Clearly, activation/amplification of the NLO response results from the formation of the octahedral supramolecular cages.¹⁸ Similarly, the hyperpolarizability γ^{19} increases on going from $[\mathbf{1}](\text{OTf})_6$ (4.73×10^{-29} esu) to $[\mathbf{2}](\text{OTf})_6$ (6.39×10^{-29} esu) and $[\mathbf{3}](\text{OTf})_6$ (6.95×10^{-29} esu) (SI, Table S3), most likely owing to the increasing π -conjugation in the ligands, as observed with organic molecules.²⁰

In conclusion, we reported a general strategy to control the degree of distortion of octahedron-type supramolecular cages by employing both coordination and covalent interactions. Through the simple addition reactions between the sulfur atoms and pyridine-substituted alkynyl ligands, followed by those of Cu(I) ions, three novel cationic cages with different degrees of distortion have been obtained and characterized by NMR spectroscopy, mass spectrometry, and single crystal X-ray crystallography. We could demonstrate that the degree of distortion of these octahedral supramolecular cages can be adjusted simply by changing the length of the rigid alkynyl-containing pyridine linkers. The cages reported in this work display obvious third-order NLO responses. The approach reported here could be extended to control the self-assembly process and the distortion of topologically fascinating structures.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c07014>.

Experimental procedures, spectroscopic data, and X-ray crystallography (PDF)

Crystallographic data of $[\mathbf{1}](\text{OTf})_6$, $[\mathbf{2}](\text{OTf})_6$, $[\mathbf{3}](\text{OTf})_6$ (CIF)

Accession Codes

Supplementary crystallographic data CCDC 2008001 ($[\mathbf{1}](\text{OTf})_6$), 2008003 ($[\mathbf{2}](\text{OTf})_6$), and 2008013 ($[\mathbf{3}](\text{OTf})_6$)

can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

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Notes

The authors declare no competing financial interest.

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