Published in final edited form as:

Inorg Chem. 2018 July 16; 57(14): 8054–8057. doi:10.1021/acs.inorgchem.8b01583.

Tetra-, Hexa-, Dodeca-Nuclear Ir Supramolecules via Bridge-Driven Self-Assembly of Tetrazolyl Ligands

Seul Gi Lee^{a,†}, Ji Yeon Ryu^{a,†}, Peter J. Stang^{*,b}, and Junseong Lee^{*,a}

^aDepartment of Chemistry, Chonnam National University, Gwangju 61186, Republic of Korea

^bDepartment of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, USA

Abstract

Herein, we report the formation of multinuclear Ir₄, Ir₆, Ir₁₂ supramolecular complexes via the bridge-driven self-assembly of tetrazolyl ligands. The synthesis of dimeric half-sandwich Ir units was made by the reaction of half-sandwich Ir units and tetrazolyl ligands in a molar ratio of 1:2. The use of different ligands containing multiple tetrazolyl units resulted in the formation of different Ir supra-molecular architectures. The reaction of [Cp*IrCl₂]₂, AgOTf, and 1,2- or 1,3-ditetrazolyl benzene in a molar ratio of 1:3:1 resulted in the formation of rectangular tetranuclear or truncated trigonal pyramidal hexanuclear Ir complexes, respectively. On the other hand, the reaction of [Cp*IrCl₂]₂, AgOTf and 1,3,5- tritetrazolyl benzene in a molar ratio of 6:18:4 produced a supramolecular dodecanuclear iridium complex. The molecular structure of the complex resembled a truncated tetrahedral structure with a large inner cavity, as determined by X-ray crystallography.

Graphical Abstract

*Corresponding Author: stang@utah.edu, leespy@chonnam.ac.kr.

†These authors contributed equally in this research.

Supporting Information

Experimental procedures, analytical data of the cages with ¹H NMR, and mass spectra of **1** – **3**. X-ray Crystallographic data for **1** – **3** are in cif format. Supporting Information is available free of charge on the ACS Publications website.

Tetra-, hexa-, and dodeca-nuclear Ir supramolecules have been synthesized from the bridge-driven self-assemblies of $[\text{Cp}^*\text{IrCl}_2]_2$ and multi-tetrazolyl benzene in the presence of AgOTf.

Since the past couple of decades, coordination-driven self-assembly based on coordination bonding between an electron accepting metal center and electron donating groups have been making significant contributions to the structural diversity and precise control of the sizes and shapes of molecules in supramolecular chemistry.^{1–12} In particular, the metal-pyridine coordination bond provided fixed coordination environments such as 90° bond angles and distances (Chart 1(a)), which facilitated the design of desired structures, and afforded various high-dimensional supramolecular architectures.^{13–17}

Recently researches have tried to extend the scope of supramolecular assemblies by using other electron donating groups such as imidazole¹⁸ and carboxylate^{19–20}. Especially, we have tried to use tetrazolyl ligands as electron donating ligands and reported interesting half-sandwich ruthenium supramolecules containing tetrazolyl units, in which they provided multi coordination sites.²¹ In that study, we found that the tetrazolyl ligand can bridge two Ru metal ions by a μ_2 -bridging mode. Murherjee's group also reported interesting Pd tetrazolyl supramolecules by using multiple binding sites of the tetrazolyl group.²² However, precise structural control of supramolecular tetrazolyl complexes has not been reported yet due to multiple binding sites of the tetrazolyl groups. Therefore, to modulate supramolecular architectures, we tried to develop simple and convenient basic connecting units composed of half-sandwich Ir groups and tetrazolyl ligands.

Ir complexes containing tetrazolyl ligands have been extensively studied^{23–24} and there are several interesting reports on the synthesis of half-sandwich Ir complexes containing one, two, or three bridging tetrazolyl ligands.^{25–26} Inspired by this, we envisioned that it is possible to construct high dimensional supramolecular architectures by preparing half-sandwich Ir tetrazolyl complexes and connecting them using phenyl rings.

Herein, we report a new bridge-driven self-assembly unit produced from dimeric Ir units containing two bridging tetrazolyl ligands. The stoichiometric reaction of a half-sandwich Ir complex and a tetrazolyl ligand in a molar ratio of 1:2 produces the basic connecting fragment, in which two half-sandwich Ir units are joined by two tetrazolyl ligands and a Cl ion. (Chart 1(b)) The two tetrazolyl units in the dimeric Ir unit have a connection angle of 120°, and differences in the position and number of tetrazolyl ligands lead to different complexation features.

To apply this concept in the supramolecular assembly, we designed and synthesized di- and tri-tetrazolyl ligands. Three different types of tetrazolyl units were prepared and used for the construction of iridium supramolecules. (Chart 2)

First, 1,2-ditetrazolylbenzene (H_2LI) was used in the assembly. Chelation of the tetrazolyl ligands was expected because the two tetrazolyl units were close to each other. The reaction of $[\text{Cp}^*\text{IrCl}_2]_2$, H_2LI , and AgOTf was conducted in methanol (Scheme 1a). The initial mixture showed a complicated ¹H NMR spectrum. Crystals suitable for X-ray crystallography were obtained by simple crystallization, and the molecular structure was

confirmed as tetranuclear Ir rectangular complex **1**. (Figure 1) The ^1H NMR spectrum also indicated the formation of complex **1**. ESI-MS analysis also confirmed the stoichiometry of Ir complex **1** in solution. The mass spectrum of **1** exhibited peaks at $m/z = 1953.77$, corresponding to $[\mathbf{1} - \text{OTf}]^+$. (Figure S7 in the Supporting Information)

The molecular structure of **1** includes four Cp^*Ir units, two chloride ions, and two **L1** ligands. There are two types of Ir metal centers in the molecular structure of **1**, each having a different coordination environment. Two Ir metal centers of the first type are tetra-coordinated with the two N atoms of **L1** via a $\kappa^2\text{-N}_2$ binding mode, a chloride ion, and Cp^* ring. The other two Ir metal centers are tetra-coordinated with two N atoms of two different **L1** ligands in a $\mu\text{-}\kappa^1(\text{N}), \kappa^1(\text{N}')$ binding mode, a chloride ion, and a Cp^* ring. Because of the short distance between the two tetrazolyl groups, chelation of di-tetrazolyl benzene was observed in complex **1**, instead of the dimeric Ir units possessing two bridging tetrazolyl groups. In the chelation of the two tetrazolyl units, the two tetrazolyl units are not parallel to the phenyl plane but twisted by 41 and 49 degrees in compound **1**.

In order to prevent the possible chelating modes of two tetrazolyl units and to obtain a dimeric Ir system possessing two bridging tetrazolyl groups, 1,3- ditetrazolyl benzene (**H₂L2**) was used in the reaction instead of the 1,2-anaolgue. (Scheme 1b) The reaction of $[\text{Cp}^*\text{IrCl}_2]_2$, **H₂L2**, and AgOTf in molar ratios of 1:1:3 produced trigonal pyramidal supramolecule **2**. The ^1H NMR spectrum indicated the formation of hexanuclear Ir complex **2**. ESI-MS analysis also confirmed the formation of Ir complex **2** in solution, exhibiting peaks at $m/z = 902.64$, corresponding to $[\mathbf{2} - 3\text{OTf}]^{3+}$. (Figure S8 in the Supporting Information) Its structure was determined by X-ray crystallography (Figure 2).

Compound **2** was confirmed to have six Cp^*Ir half sandwich units, three chloride ions and three **L2** ligands. As expected, the two iridium metal centers are bridged by two tetrazolyl units and one chloride ion with the chelated half-sandwich Ir units. The three Cp^*Ir dimeric units are tilted about 35° to the center of the supramolecule. Therefore, the three half-sandwich Ir units are close to each other, with Ir-Ir distances of about 9.4 Å. In contrast, the other three Ir centers have longer Ir-Ir distances (ca. 12.8 Å). Considering these three units and ligand **L2**²⁻ as edges and faces, respectively, the architecture of compound **2** can be considered as a truncated trigonal pyramid.

To obtain predesigned three-dimensional supramolecules, ligand **H₃L3** containing three tetrazolyl groups was used. The reaction of $[\text{Cp}^*\text{IrCl}_2]_2$, **H₃L3**, and AgOTf in a molar ratio 6:4:18 was carried out in DMSO. (Scheme 2) The presence a singlet at 8.2 ppm corresponding to phenyl group of tetrazolyl ligands in ^1H NMR indicated the formation of a symmetrical single product. ESI-MS analysis also confirmed the stoichiometry of Ir supramolecule **3** in solution. The mass spectrum of **3** exhibited peaks at $m/z = 1389.40$, 1081.80, and 876.52, corresponding to $[\mathbf{3} - 4\text{OTf}]^{4+}$, $[\mathbf{3} - 5\text{OTf}]^{5+}$ and $[\mathbf{3} - 6\text{OTf}]^{6+}$, respectively with the isotropic distributions. (Figure S9 in the Supporting Information) Crystallization of the reaction mixture produced crystalline compound **3**. X-ray crystallography data confirmed its molecular structure to be a truncated tetrahedron. (Figure 3)

Compound **3** has twelve Cp*Ir half sandwich units, four $L3^{3-}$ ligands, and six triflate ions. The Ir metal centers are coordinated with the Cp ring, two nitrogen atoms of two tetrazolyl units, and one chloride ion. The tetrazole-Ir2-tetrazole angles are about 72°. The distances between the center of the molecule and the phenyl rings are about 5.4 Å. From this distance, the volume of the inscribed sphere is calculated as 670 Å³, which indicates sufficient space for the possible inclusion of small organic molecules or ions.

Although the ideal interplanar angles between the tetrazolyl groups connected by two Ir metal centers are 120°, compounds **2** and **3** have relatively small interplanar angles (104° and 98°, respectively). This indicates that the bridging tetrazolyl ligand is flexible and may provide stability to the assembled architectures.

In conclusion, the formation of half-sandwich dimeric Ir complexes connected by tetrazolyl ligands proved to be an efficient method for the formation of various novel Ir supramolecules. Moreover, multi-tetrazolyl ligands played an important role in the formation of the supramolecular architectures: 1,2- and 1,3-Ditetrazolyl benzene provided rectangular and truncated trigonal pyramidal Ir supramolecules, respectively. The truncated tetrahedral supramolecule, which contains 12 half-sandwich Ir units, was prepared by using 1,3,5-tritetrazolyl benzene. We believe that this bridge-driven self-assembly may serve as a convenient concept for the construction of other concrete supramolecules. Future work will focus on the structural variation of Ir supramolecules by varying the number of bridging tetrazolyl units or by the use of alkyl tetrazolyl ligands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

J.L. acknowledges financial support from Basic Science Research Program (2016R1D1A1B03930507) and BRL Program (2015R1A4A1041036) of the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT & Future Planning and Education. P.J.S. thanks the NIH(R01-CA215157) for financial support.

REFERENCES

- (1). Brown CJ; Toste FD; Bergman RG; Raymond KN Supramolecular Catalysis in Metal-Ligand Cluster Hosts. *Chem. Rev* 2015, 115, 3012–3035. [PubMed: 25898212]
- (2). McConnell AJ; Wood CS; Neelakandan PP; Nitschke JR Stimuli-Responsive Metal–Ligand Assemblies. *Chem. Rev* 2015, 115, 7729–7793. [PubMed: 25880789]
- (3). Saalfrank RW; Maid H; Scheurer A Supramolecular Coordination Chemistry: The Synergistic Effect of Serendipity and Rational Design. *Angew. Chem. Int. Ed* 2008, 47, 8794–8824.
- (4). Oliveri CG; Ulmann PA; Wiester MJ; Mirkin CA Heteroligated Supramolecular Coordination Complexes Formed via the Halide-Induced Ligand Rearrangement Reaction. *Acc. Chem. Res* 2008, 41, 1618–1629. [PubMed: 18642933]
- (5). Fujita D; Ueda Y; Sato S; Mizuno N; Kumasaka T; Fujita M Self-assembly of tetravalent Goldberg polyhedra from 144 small components. *Nature* 2016, 540, 563–566.
- (6). Harris K; Fujita D; Fujita M Giant hollow MnL_{2n} spherical complexes: structure, functionalisation and applications. *Chem. Commun* 2013, 49, 6703–6712.

- (7). Sun W-Y; Kusakawa T; Fujita M Electrochemically Driven Clathration/Declathration of Ferrocene and Its Derivatives by a Nanometer-Sized Coordination Cage. *J. Am. Chem. Soc* 2002, 124, 11570–11571. [PubMed: 12296702]
- (8). Neelakandan PP; Jimenez A; Nitschke JR Fluorophore incorporation allows nanomolar guest sensing and white-light emission in M4L6 cage complexes. *Chem. Sci* 2014, 5, 908–915.
- (9). Gianneschi NC; Masar MS; Mirkin CA Development of a Coordination Chemistry-Based Approach for Functional Supramolecular Structures. *Acc. Chem. Res* 2005, 38, 825–837. [PubMed: 16285706]
- (10). Saha ML; Schmittel M From 3-Fold Complete Self-Sorting of a Nine-Component Library to a Seven-Component Scalene Quadrilateral. *J. Am. Chem. Soc* 2013, 135, 17743–17746. [PubMed: 24224927]
- (11). Seidel SR; Stang PJ High-symmetry coordination cages via self-assembly. *Acc. Chem. Res* 2002, 35, 972–983. [PubMed: 12437322]
- (12). Caulder DL; Raymond KN Supermolecules by Design. *Acc. Chem. Res* 1999, 32, 975–982.
- (13). Caulder DL; Bruckner C; Powers RE; König S; Parac TN; Leary JA; Raymond KN Coordination number incommensurate cluster formation, part 21 - Design, formation and properties of tetrahedral M4L4 and M4L6 supramolecular clusters. *J. Am. Chem. Soc* 2001, 123, 8923–8938. [PubMed: 11552799]
- (14). Smulders MMJ; Riddell IA; Browne C; Nitschke JR Building on architectural principles for three-dimensional metallosupramolecular construction. *Chem. Soc. Rev* 2013, 42, 1728–1754. [PubMed: 23032789]
- (15). Cook TR; Stang PJ Recent Developments in the Preparation and Chemistry of Metallacycles and Metallacages via Coordination. *Chem. Rev* 2015, 115, 7001–7045. [PubMed: 25813093]
- (16). Leininger S; Olenyuk B; Stang PJ Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chem. Rev* 2000, 100, 853–908. [PubMed: 11749254]
- (17). Jiang B; Zhang J; Ma J-Q; Zheng W; Chen L-J; Sun B; Li C; Hu B-W; Tan H; Li X; Yang H-B Vapochromic Behavior of a Chair-Shaped Supramolecular Metallacycle with Ultra-Stability. *J. Am. Chem. Soc* 2016, 138, 738–741. [PubMed: 26741405]
- (18). Samanta D; Mukherjee PS Component Selection in the Self-Assembly of Palladium(II) Nanocages and Cage-to-Cage Transformations. *Chem. Eur. J* 2014, 20, 12483–12492. [PubMed: 25111071]
- (19). Chakrabarty R; Mukherjee PS; Stang PJ Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev* 2011, 111, 6810–6918. [PubMed: 21863792]
- (20). Zhang M; Saha ML; Wang M; Zhou Z; Song B; Lu C; Yan X; Li X; Huang F; Yin S; Stang PJ Multicomponent Platinum(II) Cages with Tunable Emission and Amino Acid Sensing. *J. Am. Chem. Soc* 2017, 139, 5067–5074. [PubMed: 28332834]
- (21). Park YJ; Ryu JY; Begum H; Lee MH; Stang PJ; Lee J Selective Formation of Heterometallic Ru–Ag Supramolecules via Stoichiometric Control of Multiple Different Tectons. *J. Am. Chem. Soc* 2015, 137, 5863–5866. [PubMed: 25910509]
- (22). Howlader P; Mukherjee PS Face and edge directed self-assembly of Pd12 tetrahedral nano-cages and their self-sorting. *Chem. Sci* 2016, 7, 5893–5899. [PubMed: 30034731]
- (23). Monti F; Baschieri A; Gualandi I; Serrano-Pérez JJ; Junquera-Hernández JM; Tonelli D; Mazzanti A; Muzzioli S; Stagni S; Roldan-Carmona C; Pertegás A; Bolink HJ; Ortí E; Sambri L; Armaroli N Iridium(III) Complexes with Phenyl-tetrazoles as Cyclometalating Ligands. *Inorg. Chem* 2014, 53, 7709–7721. [PubMed: 25004160]
- (24). Umamahesh B; Karthikeyan NS; Sathiyarayanan KI; Malicka JM; Cocchi M Tetrazole iridium(III) complexes as a class of phosphorescent emitters for high-efficiency OLEDs. *J. Mater. Chem. C* 2016, 4, 10053–10060.
- (25). Kotera M; Sekioka Y; Suzuki T Structural Versatility of 5-Methyltetrazolato Complexes of (η⁵-Pentamethylcyclopentadienyl)iridium(III) Incorporating 2,2'-Bipyridine, N,N-Dimethyldithiocarbamate, or 2-Pyridinethiolate Ligands. *Inorg. Chem* 2008, 47, 3498–3508. [PubMed: 18041830]

- (26). He F; Ruhlmann L; Gisselbrecht J-P; Choua S; Orio M; Wesolek M; Danopoulos AA; Braunstein P Dinuclear iridium and rhodium complexes with bridging arylimidazolidine-N3,C2 ligands: synthetic, structural, reactivity, electrochemical and spectroscopic studies. Dalton Trans. 2015, 44, 17030–17044. [PubMed: 26226202]

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 1.

Ball-and-stick representation of the X-ray structure of Ir supramolecule **1**: front (top), top (bottom right), and side (bottom left) with different-color views. H atoms and counterions are omitted for clarity. Color code: Ir, blue; N, sky blue; O, red; C, gray; Cl, green.

(a)

(b)

(c)

Figure 2.

Ball-and-stick representation of the X-ray structure of Ir supramolecule **2**: front (top), top (middle), and front without Cp* ring with structural frame representation (bottom left) and different-color views. H atoms and counterions are omitted for clarity. Color code: Ir, blue; N, sky blue; O, red; C, gray; Cl, green.

Figure 3. Ball-and-stick representation of the X-ray structure of Ir supramolecule **3**: (a) front (top), (b) back (middle), and (c) front without the Cp* ring with structural frame representation (bottom left) and different-color views. H atoms and counterions are omitted for clarity. Color code: Ir, blue; N, sky blue; O, red; C, gray; Cl, green.

Chart 1.

Comparison of (a) Coordination-Driven and (b) Bridge-Driven Self-Assemblies.

Chart 2.

(a) 1,2-, (b) 1,3- Ditetrazolyl Benzene and (c) 1,3,5-Tritetrazoyl Benzene as Bridging Tetrazolyl Units.

Scheme 1.

Syntheses of (a) Tetranuclear Ir Complex **1** and (b) Hexanuclear Ir Complex **2**.

Scheme 2.
Synthesis of Dodecanuclear Ir Supramolecule **3**.