Published in final edited form as:

J Am Chem Soc. 2019 August 21; 141(33): 13187–13195. doi:10.1021/jacs.9b05682.

Combining Synthesis and Self-Assembly in One Pot To Construct Complex 2D Metallo-Supramolecules Using Terpyridine and Pyrylium Salts

Heng Wang[†], Yiming Li[†], Hao Yu[‡], Bo Song[†], Shuai Lu^{†,§}, Xin-Qi Hao[§], Yuan Zhang^{||}, Ming Wang[‡], Saw-Wai Hla^{||}, Xiaopeng Li^{*,†}

[†]Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

[‡]State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, Jilin 130012, China

[§]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450001, China

^{||}Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois 60439, United States

Abstract

Multicomponent self-assembly in one pot provides an efficient way for constructing complex architectures using multiple types of building blocks with different levels of interactions orthogonally. The preparation of multiple types of building blocks typically includes tedious synthesis. Here, we developed a multicomponent synthesis/self-assembly strategy, which combined covalent interaction (C—N bond, formed through condensation of pyrylium salt with primary amine) and metal–ligand interaction (N → Zn bond, formed through 2,2':6',2''-terpyridine–Zn coordination) in one pot. The high compatibility of this pair of interactions smoothly and efficiently converted three and four types of components into the desired complex structures, which are supramolecular Kandinsky Circles and spiderwebs, respectively.

Graphical Abstract

*Corresponding Author xiaopenglil@usf.edu.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.9b05682](https://doi.org/10.1021/jacs.9b05682).

Synthetic details, molecular modeling, ligand and complex characterization, including ¹H NMR, ¹³C NMR, 2D COSY, 2D NOESY, 2D DOSY, ESI–MS, and TWIM–MS, and additional TEM and STM images (PDF)

The authors declare no competing financial interest.

INTRODUCTION

Nature, as a talent programmer, codes extremely sophisticated life information into proteins and DNAs through combining multicomponent *in situ* reactions with multilevel noncovalent (hydrogen bonding, π - π , dipole-dipole, etc.) and covalent (amidations or esterifications) interactions in one biological system.¹ Formation of discrete assemblies from a pool of building block through “order-out-of-chaos” approaches is emerging as one of the ultimate goals of synthetic supramolecular chemistry in pursuing a higher level of complexity and desired functionalities.² Among the diverse research fields of supramolecular chemistry, coordination-driven self-assembly benefiting from its highly directional and predictable feature has been extensively applied to construct a vast variety of supramolecular architectures,³ including helicates,⁴ grids,⁵ rotaxanes,⁶ catenanes,⁷⁻⁹ links,¹⁰ knots,¹¹ polygons,¹²⁻¹⁴ and polyhedra.¹⁵⁻¹⁷ However, most of these studies focused on building metallo-supramolecules via a single type of organic building block.

To achieve more sophisticated supramolecular systems with higher efficiency, great efforts have been made on multicomponent self-assembly, such as social self-sorting to compose a series of heteroleptic coordination sites,^{16e,18-20} subcomponent self-assembly based on reversible imine bond formation and metal-ligand coordination,^{17f,g,21} template-driven synthesis of discrete supramolecules,^{22,23} etc. These one-pot strategies rather than combining all building blocks in a presynthesized ligand dramatically reduced the barrier in ligand design and synthesis. However, rational design of different levels of interactions in an orthogonal manner to minimize unwanted products is still full of challenges in the multicomponent system, and thus limits the complexity of metallo-supramolecules for further advancement of functionality.

Beyond those boundaries, we herein developed a multicomponent synthesis/self-assembly strategy, which enabled the construction of double layered supramolecular Kandinsky Circles (**KC**) with three components, and supramolecular spiderwebs with four components in one pot. Unlike subcomponent and template-driven synthetic strategies, such an attempt combined an irreversible condensation of pyrylium salt and primary amine²⁴ together with highly reversible 2,2':6',2''-terpyridine (tpy)-Zn(II) coordination processes²⁵ in one pot without any assistance from templates. This new approach not only improved the synthetic

efficiency of desired supramolecules with increasing complexity, but also enriched the library of the multicomponent self-assembly.

RESULTS AND DISCUSSION

Self-Assembly of Double Layered KC via One-Pot Strategy.

In our previous work, we assembled multilayered **KC**s using multitopic tpy-pyridinium salts through multistep synthesis.^{14j,k} Such **KC**s exhibited remarkable antimicrobial activity against Gram-positive pathogen methicillin-resistant *Staphylococcus aureus* (MRSA). However, the tedious synthesis and challenging purification of the charged multiarmed tpy-pyridinium ligands limited the investigations of their properties and applications. As a result, instead of using the conventional strategy (Scheme 1a), we tried to explore the possibility of directly constructing **KC** through two precursors, which are pyrylium salt **A** and primary amine **B**, with the proper portion of Zn(II) in one pot (Scheme 1b). We hypothesized that the condensation and the tpy-Zn coordination could be orthogonal to facilitate this new type of in situ multicomponent synthesis/self-assembly. We speculated the following three circumstances might occur: (i) no condensation happens, and a mixture of numerous monolayered circles is assembled by **A/B** with Zn(II) narcissistically or socially; (ii) condensation partially occurs, and a mixture of ligand **L1** and unreacted **A/B** forms random polymeric metallo-assemblies; and (iii) **A** and **B** are fully converted, and the multicomponent synthesis/assembly perfectly generates a desired discrete structure.

Precursors **A/B** and Zn(NO₃)₂ were mixed in DMSO with the stoichiometric ratio (1/1/2). After 24 h of heating at 110 °C, the assembly was precipitated by adding an excess amount of NH₄PF₆ methanol solution, collected after simple methanol wash, and directly subjected for characterization without further purification. Electrospray ionization–mass spectrometry (ESI–MS) was first utilized to address the molecular composition of the obtained assembly. The mass spectrum (Figure 1a) shows one dominant set of peaks with continuous charge states from 11+ to 24+, suggesting a discrete supramolecular structure was obtained during the one-pot synthesis/self-assembly. After deconvolution of each peak, the measured molecular mass of the obtained supramolecule was 17 413 Da on average, which exactly matches the molecular composition of **KC** [C₈₄₆H₇₃₂O₁₈N₇₈Zn₁₂P₃₀F₁₈₀]. The experimental isotope pattern of each charge state also agrees well with the theoretical simulation based on the chemical composition of **KC** (Figure 1, inset, and Figure S33). Traveling wave ion mobility-mass spectrum (TWIM-MS)^{14k,26} presents a series of signals with narrow bands attributed to **KC** species with successive charge state, indicating high isomeric purity of the composed structure. NMR spectra including ¹H, COSY, and NOESY were collected (Figures S5–11) and carefully compared to the results collected from the supramolecule assembled via presynthesized ligand strategy.^{14j} No significant difference was observed between the supramolecules prepared through these two strategies (Figure S5), suggesting that the condensation and coordination were compatible and orthogonal in such a one-pot manner.

Carefully identifying the compositions among the reaction mixture at each reaction stage offered us more detailed information on understanding the mechanism of the *in situ*

synthesis and self-assembly. ESI-MS was utilized to monitor the assembly process, and the results are shown in Figure 2. At the earliest reaction stage (15 min after the reaction mixture was heated at 110 °C, to dissolve all reactants), an extremely messy spectrum was observed with most peaks in the range of m/z 500–900, but no peak was detected for **KC**. Detailed analysis of these peaks indicated that a mixture of **B**-Zn(II) macrocycles and **A-B**-Zn(II) macrocycles was formed at the very beginning of the self-assembly (Figure S41a,b and Scheme S3a). Intriguingly, **A-B** condensation intermediate, [**A-B**] (structure was shown in Scheme S3b), was found to be assembled with Zn(II) along with various amounts of additional **A** and/or **B** (Figure S41c,d and Scheme S3b,c). Such multiple entities were regarded as the intermediate species prior to the formation of our desired **KC** structure. After 2 h of heating, several peaks assigned to **KC** were observed and gradually enhanced with increasing reaction time. As compared to the rising of the sharp peaks of **KC**, all of the other messy peaks shrank and completely disappeared after 24 h of heating, indicating a complete conversion of **A/B** to form **KC** (Figure 2).

We gradually lowered the temperature from 110 to 50 °C to monitor the conversion process using ESI-MS, which showed a significant increase of full conversion time (Figures S42-44). The full conversion time for each reaction temperature is 24 h at 110 °C, 60 h at 90 °C, 164 h at 70 °C, and 456 h at 50 °C. Along with the conversion of the intermediate species, clean sets of peaks of **KC** were observed under all temperature conditions without other impurities observed.

Self-Assembly of Spiderweb-Like Supramolecules (SW-1 and SW-2) via One-Pot Strategy.

To test the versatility of this new one-pot strategy, we could design even more complex supramolecules by simply changing organic precursors. For instance, a spiderweb-like (**SW-1**) supramolecule can be constructed by replacing precursor **B** with a tritopic tpy ligand **C** and adding hexatopic tpy ligand **D** as a core in a four-component synthesis/self-assembly (Scheme 2a). **SW-1** was constructed by using the same procedure of preparing **KC**. Only one dominant set of sharp peaks is observed in the ESI-MS spectrum (Figure 3) with various charge states (11+ to 24+). The isotope pattern of each charge state peak also agrees well with the corresponding theoretical simulation result (Figure 3, inset, and Figure S34). The averaged molecular mass was deconvoluted as 21 508 Da, which matches the chemical composition ($C_{996}H_{678}N_{114}Zn_{18}P_{42}F_{252}$). Furthermore, TWIM-MS spectrum shows a series of narrowly distributed signals, indicating no isomers or conformers were formed during the self-assembly. Collision cross sections (CCSs),^{26b,c} which are determined by the shape and size of molecules, are derived through the drift time of **SW-1** species with various charge states (results are summarized in Table S2 and Figure S48). The averaged measured CCS is 2817.0 Å², which is in good agreement with the calculated CCS result (2826.9 Å²) of **SW-1**. Note that the CCS of **SW-1** is slightly larger than that of **KC** (2466 Å²).^{14j} The excess CCS value should come from the additional core structure of **SW-1** as compared to **KC**. Further stability characterization in the gas phase was carried out by gradient tandem mass spectrometry (gMS²)²⁶ under various collision energies, as shown in Figure S39. The 15+ ions of **SW-1** totally dissociated at 40 V, corresponding to a center-of-mass collision energy at 0.08 eV. The dissociation voltage is much higher than the corresponding total dissociation voltage of 15+ ions of **KC** (30 V, center-of-mass collision energy at 0.07 eV, Figure S38),

indicating a higher stability of **SW-1** than of **KC** (in gas phase). Such enhanced stability is attributed to the higher density of coordination sites (DOCS) of **SW-1** (0.0064 site/Å²) than of **KC** (0.0047 site/Å²).²⁷

Apart from the one-pot strategy, another stepwise approach was also employed to construct **SW-1**. The stepwise approach was illustrated in Scheme S2. Precursors **C** and **D** were assembled with a stoichiometric amount of Zn(II) to produce a discrete supramolecular spokedwheel (**SW-3**)²⁸ with six reactive amino groups around the rim. ESI-MS of **SW-3** (Figure S36) displays one dominant set of sharp peaks with continuous charges from 8+ to 18+, as well as well-resolved isotope patterns (Figure S37). The deconvoluted molar mass is 12 733 Da, matching its chemical composition. Precursor **A** and an additional amount of Zn(II) were added into the **SW-3** solution. ESI-MS showed that **SW-1** was smoothly formed with the similar ESI-MS spectrum as the one-pot method (Figure S45). Such results further support the high orthogonality of the tpy-Zn(II) coordination with the condensation reaction.

Figure 4 shows the ¹H NMR spectra of **SW-1** and **SW-3**, which provide more detailed structural information. In the spectra of **SW-3**, three sets of peaks assigned to the protons on the tpy groups can be figured out, corresponding to the three different chemical environments of coordination sites in the supramolecule, with one on the outer rim edge, and two on the spoke. Characteristic upfield shifts of all a, b, c6,6'' are exhibited on the spectrum by comparing with the metal free tpy contained ligands (Figures S1, S3, and S4).^{14k,28} In the spectrum of **SW-1** (Figure 4a), the characteristic peak of amino protons of **SW-3** shown around 5.4 ppm disappears; meanwhile, the new peak assigned to H^f of pyridinium ring and the obvious downfield shift of H^f together prove the full conversion of the amino group to pyridinium group, during the formation of **SW-1**. Four sets of tpy protonic peaks are exhibited in the spectrum, corresponding to the additional layer of hexagonal ring by comparison with **SW-3**. Again, the characteristic high field a-d6,6'' protonic signals are displayed, indicating the full coordination of tpy groups with Zn(II) ions. In addition, all peaks of **SW-1** inner layer protons (H^{A-H}, a,b,c-tpy-H) locate in a much higher magnetic field area as compared to the corresponding signals of **SW-3**, which could be attributed to the electron shielding effect from the hexagonal outer rim on these inner ring protons. A 2D diffusion-ordered NMR spectroscopy (2D-DOSY) analysis in d₆-DMSO reveals a single band at log *D* ≈ -10.5 (Figure S30), corresponding to a discrete architecture. For comparison, the measured log *D* value of **SW-3** is ca. -10.3 (Figure S32), corresponding to its much smaller diameter as compared to that of **SW-1**. Using the modified Stocks-Einstein equation based on the oblate spheroid model (see the Supporting Information for details),²⁹ the experimental radii or the semimajor radii of **SW-1** and **SW-3** were calculated as 4.1 and 2.6 nm, which are comparable to the results obtained from theoretical models (3.9 nm shown in Figure 6c, and 2.8 nm shown in Figure S54). The other NMR spectroscopic results are summarized in the Supporting Information, including 2D COSY, 2D NOESY, and ¹³C NMR spectra (Figures S12-S29).

Transmission electron microscopy (TEM) was further utilized to visualize individual supramolecules. Under TEM imaging, a series of dots with narrowly dispersed diameters was observed (Figure S50a). The zoomed-in image of one dot shows a hexagon flake shape with the measured diameter as ca. 7.0 nm, which is consistent with the molecular modeling

result (Figure 6c). To obtain a higher resolution image of **SW-1**, ultrahigh-vacuum, low-temperature scanning tunneling microscopy (UHV-LT-STM) was utilized to study the supramolecules on Ag(111) surface. As shown in Figure 6a,b and Figure S51, a high density of individual **SW-1** molecules are observed on the surface with hexagram shape, and the diameter of each hexagram is also around 7.0 nm (Figure 6a). Note that the bright dots in each hexagram represent $\langle \text{tpy-Zn(II)-tpy} \rangle$ units due to their octahedral coordination structure and higher electron density around the metal ions. Two layers of bright lobes, which are a hexagonal outer rim and a hexagonal inner ring, can be clearly observed in Figure 6b. The larger lobes on the outer rim are assigned to the two layers of $\langle \text{tpy-Zn(II)-tpy} \rangle$ units with their signals merged together, while the smaller ones in the inner ring are attributed to the $\langle \text{tpy-Zn(II)-tpy} \rangle$ junctions linked to the hexatopic core (ligand **D**).

In addition to the hexatopic tpy ligand **D**, two tritopic tpy ligands **E** can act together as the cores to form another discrete supramolecular spiderweb (**SW-2**) with four-component synthesis/self-assembly in one pot, that is, **A/C/D/Zn**, as shown in Scheme 2b.³⁰ The ESI-MS spectrum of the resulted product (Figure 5) proves the structure with desired chemical composition ($\text{C}_{1002}\text{H}_{684}\text{N}_{114}\text{Zn}_{18}\text{P}_{42}\text{F}_{252}$), by displaying a series of sharp peaks with average measured molecular mass as 21 585 Da. The experimental isotope patterns of each charge state are consistent with their corresponding theoretical ones (Figure 5, inset, and Figure S35). TWIM-MS spectrum of **SW-2** also exhibits a narrowly distributed set of signal bands, corresponding to an averaged experimental CCS value as $2765.0 \text{ \AA}^2$, in good agreement with the average theoretical CCS value of $2761.8 \text{ \AA}^2$ (as shown in Table S2 and Figure S49). The total dissociation voltage of **SW-2** was measured with the same value as **SW-1** in gMS² spectra (40 V, Figure S40), due to their similar DOCS values. The ¹H NMR spectrum of **SW-2** shows signals similar to that of **SW-1** (Figures S18-S23) with four sets of tpy protonic resonance signals assigned to the four different chemical environments of tpy-Zn(II) coordination sites. The 2D-DOSY spectrum of **SW-2** reveals a single band of signals with the same log *D* value of **SW-1** at ca. -10.5 (Figure S31) with calculated radius as 4.1 nm (Figure 6f). TEM and STM images of **SW-2** (Figure 6d,e, and Figures S50b and S52) also clearly show hexagonal shaped flakes of individual supramolecule with narrowly dispersed diameter at ca. 7.0 nm, further documenting the formation of the desired structure. The zoomed-in STM image of **SW-2** (Figure 6d) also shows the pattern with six larger signal lobes arranged in the outer rim of a hexagon, and a triangular pattern in the inner ring. The observed inner patterns are attributed to the three coordination junctions attached to the upper level of the tritopic core (ligand **E**), while the lower level of the core cannot be detected by the tip.

With such a new strategy in hand, we further explored the selectivity of a more complicated system, that is, selective assembly of **SW-1** in the system containing precursors **A/C/D/E** and metal ions Zn(II) with the molar ratio 6/6/1/2/18, as illustrated in Scheme 3a. Instead of forming a pool of mixtures, the self-assembly involving five components precisely picked up **A/C/D/Zn(II)** with stoichiometric ratio to form pure **SW-1**. The ESI-MS spectrum of the obtained assembled product displays only one dominant set of sharp peaks, which exactly matches the chemical composition of **SW-1** (Figure S46). Furthermore, complete core exchange was conducted by mixing equal amounts of **SW-2** and hexatopic ligand **D** at

110 °C (Scheme 3b). Yet such an exchange procedure could not occur reversely by adding 2 equiv of **E** into **SW-1** solution. Increasing the amount of **E** could only partially convert **SW-1** to **SW-2** with unidentified assemblies as revealed by the messy ESI–MS spectrum (Figure S47). All of these results suggest that **SW-1** is a more energy favorable structure as compared to **SW-2**. In this multicomponent system, a self-recognition was realized in the competition between **D** and **E**.

CONCLUSIONS

We demonstrate here a novel *in situ* multicomponent synthesis/self-assembly strategy by combining the irreversible pyrylium salt-primary amine condensation and the highly reversible tpy-Zn coordination, in an orthogonal way. A double layered supramolecular Kandinsky Circle and two supramolecular spiderwebs were constructed through the three-component and four-component synthesis/self-assembly in one pot with high efficiency. It reveals that this one-pot strategy is a thermodynamically controlled process through monitoring the reaction procedure, as well as studying the core sorting/exchange behavior between **SW-1** and **SW-2** systems. Our endeavors expand the scope of the *in situ* synthesis/self-assembly strategies from highly reversible reactions to irreversible ones. This new method can emerge as a powerful approach in building sophisticated supramolecular structures with high efficiency.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (CHE-1506722) and the National Institutes of Health (R01GM128037). Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. We also acknowledge partial support by the University of South Florida Interdisciplinary NMR facility, and through a University of South Florida Nexus Initiative (UNI) Award.

REFERENCES

- (1). Alberts B; Johnson A; Lewis J; Raff M; Roberts K; Walter P Molecular Biology of the Cell, 6th ed.; Garland Science: New York, 2014.
- (2). Whitesides GM; Grzybowski B Self-Assembly at All Scales. *Science* 2002, 295 (5564), 2418–2421. [PubMed: 11923529]
- (3) (a). Leininger S; Olenyuk B; Stang PJ Self-Assembly of Discrete Cyclic Nanostructures Mediated by Transition Metals. *Chem. Rev* 2000, 100 (3), 853–908. [PubMed: 11749254] (b)Chakrabarty R; Mukherjee PS; Stang PJ Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev* 2011, 111 (11), 6810–6918. [PubMed: 21863792] (c)Cook TR; Stang PJ Recent Developments in the Preparation and Chemistry of Metallacycles and Metallacages via Coordination. *Chem. Rev* 2015, 115 (15), 7001–7045. [PubMed: 25813093]
- (4) (a). Hasenknopf B; Lehn J-M; Kneisel BO; Baum G; Fenske D Self-Assembly of a Circular Double Helicate. *Angew. Chem., Int. Ed. Engl* 1996, 35 (16), 1838–1840.(b)Hasenknopf B; Lehn J-M; Boumediene N; Dupont-Gervais A; Van Dorsselaer A; Kneisel B; Fenske D Self-Assembly of Tetra- and Hexanuclear Circular Helicates. *J. Am. Chem. Soc* 1997, 119 (45), 10956–10962. (c)Hasenknopf B; Lehn J-M; Boumediene N; Leize E; Van Dorsselaer A Kinetic and

Thermodynamic Control in Self-Assembly: Sequential Formation of Linear and Circular Helicates. *Angew. Chem., Int. Ed* 1998, 37 (23), 3265–3268.(d)Sørensen A; Castilla AM; Ronson TK; Pittelkow M; Nitschke JR Chemical Signals Turn On Guest Binding through Structural Reconfiguration of Triangular Helicates. *Angew. Chem., Int. Ed* 2013, 52 (43), 11273–11277.(e)Ayme J-F; Beves JE; Campbell CJ; Leigh DA The Self-Sorting Behavior of Circular Helicates and Molecular Knots and Links. *Angew. Chem., Int. Ed* 2014, 53 (30), 7823–7827.

- (5) (a). Bassani DM; Lehn J-M; Fromm K; Fenske D Toposelective and Chiroselective Self-Assembly of $[2 \times 2]$ Grid-Type Inorganic Arrays Containing Different Octahedral Metallic Centers. *Angew. Chem., Int. Ed* 1998, 37 (17), 2364–2367.(b)Toyota S; Woods CR; Benaglia M; Haldmann R; Wärnmark K; Hardcastle K; Siegel JS Tetranuclear Copper(I)-Biphenanthroline Gridwork: Violation of the Principle of Maximal Donor Coordination Caused by Intercalation and CH-to-N Forces. *Angew. Chem., Int. Ed* 2001, 40 (4), 751–754.(c)Barboiu M; Vaughan G; Graff R; Lehn J-M Self-Assembly, Structure, and Dynamic Interconversion of Metallosupramolecular Architectures Generated by Pb(II) Binding-Induced Unfolding of a Helical Ligand. *J. Am. Chem. Soc* 2003, 125 (34), 10257–10265. [PubMed: 12926949]
- (6) (a). Kraus T; Bud šinský M; Cva ka J; Sauvage J-P Copper(I)-Directed Formation of a Cyclic Pseudorotaxane Tetramer and Its Trimeric Homologue. *Angew. Chem., Int. Ed* 2006, 45 (2), 258–261.(b)Beyler M; Heitz V; Sauvage J-P Coordination Chemistry-Assembled Porphyrinic Catenanes. *J. Am. Chem. Soc* 2010, 132 (12), 4409–4417. [PubMed: 20199079] (c)Joosten A; Trolez Y; Collin J-P; Heitz V; Sauvage J-P Copper(I)-Assembled [3]Rotaxane Whose Two Rings Act as Flapping Wings. *J. Am. Chem. Soc* 2012, 134 (3), 1802–1809. [PubMed: 22236438] (d)Yang Y-D; Fan C-C; Rambo BM; Gong H-Y; Xu LJ; Xiang J-F; Sessler JL Multicomponent Self-Assembled Metal–Organic [3]Rotaxanes. *J. Am. Chem. Soc* 2015, 137 (40), 12966–12976. [PubMed: 26378806] (e)Leigh DA; Pirvu L; Schaufelberger F; Tetlow DJ; Zhang L Securing a Supramolecular Architecture by Tying a Stopper Knot. *Angew. Chem., Int. Ed* 2018, 57 (33), 10484–10488.
- (7) (a). Dietrich-Buchecker CO; Sauvage JP; Kintzinger JP Une Nouvelle Famille de Molecules: Les Metallo-Catenanes. *Tetrahedron Lett.* 1983, 24 (46), 5095–5098.(b)Dietrich-Buchecker CO; Sauvage JP; Kern JM Templated Synthesis of Interlocked Macrocyclic Ligands: The Catenands. *J. Am. Chem. Soc* 1984, 106 (10), 3043–3045.
- (8). Fujita M; Ibukuro F; Hagihara H; Ogura K Quantitative Self-Assembly of a [2]Catenane from Two Preformed Molecular Rings. *Nature* 1994, 367 (6465), 720–723.
- (9) (a). Freye S; Hey J; Torras-Galán A; Stalke D; Herbst-Irmer R; John M; Clever GH Allosteric Binding of Halide Anions by a New Dimeric Interpenetrated Coordination Cage. *Angew. Chem., Int. Ed* 2012, 51 (9), 2191–2194.(b)Frank M; Hey J; Balcioglu I; Chen Y-S; Stalke D; Suenobu T; Fukuzumi S; Frauendorf H; Clever GH Assembly and Stepwise Oxidation of Interpenetrated Coordination Cages Based on Phenothiazine. *Angew. Chem., Int. Ed* 2013, 52 (38), 10102–10106.(c)Frey S; Michel R; Stalke D; Pawliczek M; Frauendorf H; Clever GH Template Control over Dimerization and Guest Selectivity of Interpenetrated Coordination Cages. *J. Am. Chem. Soc* 2013, 135 (23), 8476–8479. [PubMed: 23697828] (d)Zhu R; Lübken J; Dittrich B; Clever GH Stepwise Halide-Triggered Double and Triple Catenation of Self-Assembled Coordination Cages. *Angew. Chem., Int. Ed* 2015, 54 (9), 2796–2800.
- (10) (a). Chichak KS; Cantrill SJ; Pease AR; Chiu S-H; Cave GWV; Atwood JL; Stoddart JF Molecular Borromean Rings. *Science* 2004, 304 (5675), 1308–1312. [PubMed: 15166376] (b)Beves JE; Campbell CJ; Leigh DA; Pritchard RG Tetrameric Cyclic Double Helicates as a Scaffold for a Molecular Solomon Link. *Angew. Chem., Int. Ed* 2013, 52 (25), 6464–6467. (c)Schouwey C; Holstein JJ; Scopelliti R; Zhurov KO; Nagornov KO; Tsybin YO; Smart OS; Bricogne G; Severin K Self-Assembly of a Giant Molecular Solomon Link from 30 Subcomponents. *Angew. Chem., Int. Ed* 2014, 53 (42), 11261–11265.
- (11) (a). Guo J; Mayers PC; Breault GA; Hunter CA Synthesis of a Molecular Trefoil Knot by Folding and Closing on an Octahedral Coordination Template. *Nat. Chem* 2010, 2, 218. [PubMed: 21124480] (b)Ayme J-F; Beves JE; Leigh DA; McBurney RT; Rissanen K; Schultz D A synthetic molecular pentafoil knot. *Nat. Chem* 2012, 4, 15.(c)Barran PE; Cole HL; Goldup SM; Leigh DA; McGonigal PR; Symes MD; Wu J; Zengerle M Active-Metal Template Synthesis of a Molecular Trefoil Knot. *Angew. Chem., Int. Ed* 2011, 50 (51), 12280–12284.(d)Leigh DA; Pritchard RG; Stephens AJ A Star of David Catenane. *Nat. Chem* 2014, 6, 978. [PubMed: 25343602] (e)Zhang

- L; Stephens AJ; Nussbaumer AL; Lemonnier J-F; Jur ek P; Vitorica-Yrezabal IJ; Leigh DA Stereoselective Synthesis of a Composite Knot with Nine Crossings. *Nat. Chem* 2018, 10 (11), 1083–1088. [PubMed: 30202101]
- (12) (a). Fujita M; Yazaki J; Ogura K Preparation of a Macrocyclic Polynuclear Complex, [(en)Pd(4,4'-bpy)]₄(NO₃)₈ (en = ethylenediamine, bpy = bipyridine), Which Recognizes an Organic Molecule in Aqueous Media. *J. Am. Chem. Soc* 1990, 112 (14), 5645–5647. (b) Fujita M; Nagao S; Iida M; Ogata K; Ogura K Palladium(II)-Directed Assembly of Macrocyclic Dinuclear complexes Composed of (en)Pd²⁺ and Bis(4-pyridyl)-Substituted Bidentate Ligands. Remarkable Ability for Molecular Recognition of Electron-Rich Aromatic Guests. *J. Am. Chem. Soc* 1993, 115 (4), 1574–1576.
- (13) (a). Stang PJ; Cao DH Transition Metal Based Cationic Molecular Boxes. Self-Assembly of Macrocyclic Platinum(II) and Palladium(II) Tetranuclear Complexes. *J. Am. Chem. Soc* 1994, 116 (11), 4981–4982. (b) Stang PJ; Cao DH; Saito S; Arif AM Self-Assembly of Cationic, Tetranuclear, Pt(II) and Pd(II) Macrocyclic Squares. x-ray Crystal Structure of [Pt²⁺(dppp)(4,4'-bipyridyl)²⁻OSO₂CF₃]₄. *J. Am. Chem. Soc* 1995, 117 (23), 6273–6283. (c) Stang PJ; Chen K Hybrid, Iodonium-Transition Metal, Cationic Tetranuclear Macrocyclic Squares. *J. Am. Chem. Soc* 1995, 117 (5), 1667–1668. (d) Manna J; Whiteford JA; Stang PJ; Muddiman DC; Smith RD Design and Self-Assembly of Nanoscale Organoplatinum Macrocycles. *J. Am. Chem. Soc* 1996, 118 (36), 8731–8732. (e) Stang PJ; Persky NE; Manna J Molecular Architecture via Coordination: Self-Assembly of Nanoscale Platinum Containing Molecular Hexagons. *J. Am. Chem. Soc* 1997, 119 (20), 4777–4778. (f) Ghosh K; Yang H-B; Northrop BH; Lyndon MM; Zheng Y-R; Muddiman DC; Stang PJ Coordination-Driven Self-Assembly of Cavity-Cored Multiple Crown Ether Derivatives and Poly[2]pseudorotaxanes. *J. Am. Chem. Soc* 2008, 130 (15), 5320–5334. [PubMed: 18341280] (g) Chakrabarty R; Stang PJ Post-assembly Functionalization of Organoplatinum(II) Metallacycles via Copper-free Click Chemistry. *J. Am. Chem. Soc* 2012, 134 (36), 14738–14741. [PubMed: 22917086]
- (14) (a). Chan Y-T; Li X; Yu J; Carri GA; Moorefield CN; Newkome GR; Wesdemiotis C Design, Synthesis, and Traveling Wave Ion Mobility Mass Spectrometry Characterization of Iron(II)- and Ruthenium(II)-Terpyridine Metallomacrocycles. *J. Am. Chem. Soc* 2011, 133 (31), 11967–11976. [PubMed: 21718066] (b) Sautter A; Schmid DG; Jung G; Würthner F A Triangle–Square Equilibrium of Metallosupramolecular Assemblies Based on Pd(II) and Pt(II) Corners and Diazadibenzoperylene Bridging Ligands. *J. Am. Chem. Soc* 2001, 123 (23), 5424–5430. [PubMed: 11389622] (c) You C-C; Würthner F Self-Assembly of Ferrocene-Functionalized Perylene Bisimide Bridging Ligands with Pt(II) Corner to Electrochemically Active Molecular Squares. *J. Am. Chem. Soc* 2003, 125 (32), 9716–9725. [PubMed: 12904037] (d) Schulze M; Kunz V; Frischmann PD; Würthner F A Supramolecular Ruthenium Macrocycle with High Catalytic Activity for Water Oxidation that Mechanistically Mimics Photosystem II. *Nat. Chem* 2016, 8, 576. [PubMed: 27219702] (e) Campos-Fernández CS; Clérac R; Koomen JM; Russell DH; Dunbar KR Fine-Tuning the Ring-Size of Metallacyclophanes: A Rational Approach to Molecular Pentagons. *J. Am. Chem. Soc* 2001, 123 (4), 773–774. [PubMed: 11456607] (f) Campos-Fernández CS; Schottel BL; Chifotides HT; Bera JK; Bacsa J; Koomen JM; Russell DH; Dunbar KR Anion Template Effect on the Self-Assembly and Interconversion of Metallacyclophanes. *J. Am. Chem. Soc* 2005, 127 (37), 12909–12923. [PubMed: 16159285] (g) Chifotides HT; Giles ID; Dunbar KR Supramolecular Architectures with π -Acidic 3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine Cavities: Role of Anion– π Interactions in the Remarkable Stability of Fe(II) Metallacycles in Solution. *J. Am. Chem. Soc* 2013, 135 (8), 3039–3055. [PubMed: 23414294] (h) Safarowsky C; Merz L; Rang A; Broekmann P; Hermann BA; Schalley CA Second-Order Templation: Ordered Deposition of Supramolecular Squares on a Chloride-Covered Cu(100) Surface. *Angew. Chem., Int. Ed* 2004, 43 (10), 1291–1294. (i) Jeong KS; Kim SY; Shin U-S; Kogej M; Hai NTM; Broekmann P; Jeong N; Kirchner B; Reiher M; Schalley CA Synthesis of Chiral Self-Assembling Rhombs and Their Characterization in Solution, in the Gas Phase, and at the Liquid–Solid Interface. *J. Am. Chem. Soc* 2005, 127 (50), 17672–17685. [PubMed: 16351097] (j) Wang M; Wang K; Wang C; Huang M; Hao X-Q; Shen M-Z; Shi G-Q; Zhang Z; Song B; Cisneros A; Song M-P; Xu B; Li X Self-Assembly of Concentric Hexagons and Hierarchical Self-Assembly of Supramolecular Metal–Organic Nanoribbons at the Solid/Liquid Interface. *J. Am. Chem. Soc* 2016, 138 (29), 9258–9268. [PubMed: 27379457] (k) Wang H; Qian X; Wang K; Su M; Haoyang W-W; Jiang X; Brzozowski R; Wang M; Gao X; Li Y; Xu

- B; Eswara P; Hao X-Q; Gong W; Hou J-L; Cai J; Li X Supramolecular Kandinsky Circles with High Antibacterial Activity. *Nat. Commun* 2018, 9 (1), 1815. [PubMed: 29739936]
- (15) (a). Takeda N; Umemoto K; Yamaguchi K; Fujita M A Nanometre-Sized Hexahedral Coordination Capsule Assembled from 24 Components. *Nature* 1999, 398, 794. (b) Tominaga M; Suzuki K; Kawano M; Kusakawa T; Ozeki T; Sakamoto S; Yamaguchi K; Fujita M Finite, Spherical Coordination Networks that Self-Organize from 36 Small Components. *Angew. Chem., Int. Ed* 2004, 43 (42), 5621–5625. (c) Sun Q-F; Iwasa J; Ogawa D; Ishido Y; Sato S; Ozeki T; Sei Y; Yamaguchi K; Fujita M Self-Assembled $M_{24}L_{48}$ Polyhedra and Their Sharp Structural Switch upon Subtle Ligand Variation. *Science* 2010, 328 (5982), 1144–1147. [PubMed: 20430973] (d) Fujita D; Ueda Y; Sato S; Yokoyama H; Mizuno N; Kumasaka T; Fujita M Self-Assembly of $M_{30}L_{60}$ Icosidodecahedron. *Chem* 2016, 1 (1), 91–101.
- (16) (a). Olenyuk B; Levin MD; Whiteford JA; Shield JE; Stang PJ Self-Assembly of Nanoscopic Dodecahedra from 50 Predesigned Components. *J. Am. Chem. Soc* 1999, 121 (44), 10434–10435. (b) Olenyuk B; Whiteford JA; Fechtenkötter A; Stang PJ Self-Assembly of Nanoscale Cuboctahedra by Coordination Chemistry. *Nature* 1999, 398, 796. [PubMed: 10235260] (c) Leininger S; Fan J; Schmitz M; Stang PJ Archimedean Solids: Transition Metal Mediated Rational Self-Assembly of Supramolecular-Truncated Tetrahedra. *Proc. Natl. Acad. Sci. U. S. A* 2000, 97 (4), 1380–1384. [PubMed: 10677470] (d) Kuehl CJ; Kryschenko YK; Radhakrishnan U; Seidel SR; Huang SD; Stang PJ Self-Assembly of Nanoscopic Coordination Cages of D_{3h} Symmetry. *Proc. Natl. Acad. Sci. U. S. A* 2002, 99 (8), 4932–4936. [PubMed: 11880599] (e) Yan X; Cook TR; Wang P; Huang F; Stang PJ Highly Emissive Platinum(II) Metallacages. *Nat. Chem* 2015, 7, 342. [PubMed: 25803473]
- (17) (a). Hiraoka S; Harano K; Shiro M; Ozawa Y; Yasuda N; Toriumi K; Shionoya M Isostructural Coordination Capsules for a Series of 10 Different d^5 – d^{10} Transition-Metal Ions. *Angew. Chem* 2006, 118 (39), 6638–6641. (b) Clever GH; Tashiro S; Shionoya M Light-Triggered Crystallization of a Molecular Host–Guest Complex. *J. Am. Chem. Soc* 2010, 132 (29), 9973–9975. [PubMed: 20604553] (c) Han M; Luo Y; Damaschke B; Gómez L; Ribas X; Jose A; Peretzki P; Seibt M; Clever GH Light-Controlled Interconversion between a Self-Assembled Triangle and a Rhombicuboctahedral Sphere. *Angew. Chem., Int. Ed* 2016, 55 (1), 445–449. (d) Bar AK; Chakrabarty R; Mostafa G; Mukherjee PS Self-Assembly of a Nanoscopic $Pt_{12}Fe_{12}$ Heterometallic Open Molecular Box Containing Six Porphyrin Walls. *Angew. Chem., Int. Ed* 2008, 47 (44), 8455–8459. (e) Mal P; Breiner B; Rissanen K; Nitschke JR White Phosphorus Is Air-Stable Within a Self-Assembled Tetrahedral Capsule. *Science* 2009, 324 (5935), 1697–1699. [PubMed: 19556504] (f) Riddell IA; Smulders MMJ; Clegg JK; Hristova YR; Breiner B; Thoburn JD; Nitschke JR Anion-Induced Reconstitution of a Self-Assembling System to Express a Chloride-Binding $Co_{10}L_{15}$ Pentagonal Prism. *Nat. Chem* 2012, 4, 751. [PubMed: 22914197] (g) Rizzuto FJ; Nitschke JR Stereochemical Plasticity Modulates Cooperative Binding in a $Co^{II}_{12}L_6$ Cuboctahedron. *Nat. Chem* 2017, 9, 903. [PubMed: 28837174] (h) Mosquera J; Szyszko B; Ho SKY; Nitschke JR Sequence-Selective Encapsulation and Protection of Long Peptides by a Self-Assembled $Fe^{II}_8L_6$ Cubic Cage. *Nat. Commun* 2017, 8, 14882. [PubMed: 28358028] (i) Wang M; Wang C; Hao X-Q; Li X; Vaughn TJ; Zhang Y-Y; Yu Y; Li Z-Y; Song M-P; Yang H-B; Li X From Trigonal Bipyramidal to Platonic Solids: Self-Assembly and Self-Sorting Study of Terpyridine-Based 3D Architectures. *J. Am. Chem. Soc* 2014, 136 (29), 10499–10507. [PubMed: 24978202] (j) Xie T-Z; Liao S-Y; Guo K; Lu X; Dong X; Huang M; Moorefield CN; Cheng SZD; Liu X; Wesdemiotis C; Newkome GR Construction of a Highly Symmetric Nanosphere via a One-Pot Reaction of a Tristerpyridine Ligand with Ru(II). *J. Am. Chem. Soc* 2014, 136 (23), 8165–8168. [PubMed: 24840764] (k) Kaphan DM; Levin MD; Bergman RG; Raymond KN; Toste FD A Supramolecular Microenvironment Strategy for Transition Metal Catalysis. *Science* 2015, 350 (6265), 1235–1238. [PubMed: 26785485] (l) Xie T-Z; Guo K; Guo Z; Gao W-Y; Wojtas L; Ning G-H; Huang M; Lu X; Li J-Y; Liao S-Y; Chen Y-S; Moorefield CN; Saunders MJ; Cheng SZD; Wesdemiotis C; Newkome GR Precise Molecular Fission and Fusion: Quantitative Self-Assembly and Chemistry of a Metallo-Cuboctahedron. *Angew. Chem* 2015, 127 (32), 9356–9361. (m) Zhang H; Lee J; Lammer AD; Chi X; Brewster JT; Lynch VM; Li H; Zhang Z; Sessler JL Self-Assembled Pyridine-Dipyrrolic Cages. *J. Am. Chem. Soc* 2016, 138 (13), 4573–4579. [PubMed: 26972781]
- (18) (a). Wang M; Zheng Y-R; Ghosh K; Stang PJ Metallosupramolecular Tetragonal Prisms via Multicomponent Coordination-Driven Template-Free Self-Assembly. *J. Am. Chem. Soc* 2010,

- 132 (18), 6282–6283. [PubMed: 20405914] (b)Zheng Y-R; Zhao Z; Wang M; Ghosh K; Pollock JB; Cook TR; Stang PJ A Facile Approach toward Multicomponent Supramolecular Structures: Selective Self-Assembly via Charge Separation. *J. Am. Chem. Soc* 2010, 132 (47), 16873–16882. [PubMed: 21053935]
- (19) (a). Mahata K; Schmittel M From 2-Fold Compleitive to Integrative Self-Sorting: A Five-Component Supramolecular Trapezoid. *J. Am. Chem. Soc* 2009, 131 (45), 16544–16554. [PubMed: 19860466] (b)Saha ML; Schmittel M From 3-Fold Compleitive Self-Sorting of a Nine-Component Library to a Seven-Component Scalene Quadrilateral. *J. Am. Chem. Soc* 2013, 135 (47), 17743–17746. [PubMed: 24224927] (c)Mittal N; Pramanik S; Paul I; De S; Schmittel M Networking Nanoswitches for ON/OFF Control of Catalysis. *J. Am. Chem. Soc* 2017, 139 (12), 4270–4273. [PubMed: 28273418]
- (20). Wang S-Y; Fu J-H; Liang Y-P; He Y-J; Chen Y-S; Chan Y-T Metallo-Supramolecular Self-Assembly of a Multicomponent Ditrigon Based on Complementary Terpyridine Ligand Pairing. *J. Am. Chem. Soc* 2016, 138 (11), 3651–3654. [PubMed: 26927420]
- (21) (a). Nitschke JR Construction, Substitution, and Sorting of Metallo-organic Structures via Subcomponent Self-Assembly. *Acc. Chem. Res* 2007, 40 (2), 103–112. [PubMed: 17309191] (b)Sarma RJ ; Nitschke JR Self-Assembly in Systems of Subcomponents: Simple Rules, Subtle Consequences. *Angew. Chem., Int. Ed* 2008, 47 (2), 377–380.(c)Wood CS; Ronson TK; Belenguer AM; Holstein JJ; Nitschke JR Two-Stage Directed Self-Assembly of a Cyclic [3]Catenane. *Nat. Chem* 2015, 7, 354. [PubMed: 25803475] (d)Rizzuto FJ; Ramsay WJ; Nitschke JR Otherwise Unstable Structures Self-Assemble in the Cavities of Cuboctahedral Coordination Cages. *J. Am. Chem. Soc* 2018, 140 (36), 11502–11509. [PubMed: 30114908]
- (22) (a). Kumazawa K; Biradha K; Kusakawa T; Okano T; Fujita M Multicomponent Assembly of a Pyrazine-Pillared Coordination Cage That Selectively Binds Planar Guests by Intercalation. *Angew. Chem., Int. Ed* 2003, 42 (33), 3909–3913.(b)Kubota Y; Sakamoto S; Yamaguchi K; Fujita M Guest-Induced Organization of an Optimal Receptor from a Dynamic Receptor Library: Spectroscopic Screening. *Proc. Natl. Acad. Sci. U. S. A* 2002, 99 (8), 4854–4856. [PubMed: 11959936]
- (23) (a). Bols PS; Anderson HL Template-Directed Synthesis of Molecular Nanorings and Cages. *Acc. Chem. Res* 2018, 51 (9), 2083–2092. [PubMed: 30156831] (b)Hoffmann M; Wilson CJ; Odell B; Anderson HL Template-Directed Synthesis of a π -Conjugated Porphyrin Nanoring. *Angew. Chem., Int. Ed* 2007, 46 (17), 3122–3125.(c)O'Sullivan MC; Sprafke JK; Kondratuk DV; Rinfrey C; Claridge TDW; Saywell A; Blunt MO; O'Shea JN; Beton PH; Malfois M; Anderson HL Vernier Templating and Synthesis of a 12-Porphyrin Nano-Ring. *Nature* 2011, 469, 72. [PubMed: 21209660] (d)Kondratuk DV; Perdigão LMA; Esmail AMS; O'Shea JN; Beton PH; Anderson HL Supramolecular Nesting of Cyclic Polymers. *Nat. Chem* 2015, 7, 317. [PubMed: 25970878] (e)Neuhaus P; Cnossen A; Gong JQ; Herz LM; Anderson HL A Molecular Nanotube with Three-Dimensional π -Conjugation. *Angew. Chem., Int. Ed* 2015, 54 (25), 7344–7348.(f)Cremers J; Haver R; Rickhaus M; Gong JQ; Favereau L; Peeks MD; Claridge TDW; Herz LM; Anderson HL Template-Directed Synthesis of a Conjugated Zinc Porphyrin Nanoball. *J. Am. Chem. Soc* 2018, 140 (16), 5352–5355. [PubMed: 29638125]
- (24) (a). Katritzky AR; Manzo RH Kinetics and Mechanism of the Reactions of Primary Amines with Pyrylium Cations. *J. Chem. Soc., Perkin Trans 2* 1981, No. 3, 571–575.(b)Katritzky AR; Manzo RH; Lloyd JM; Patel RC Mechanism of the Pyrylium/Pyridinium Ring Interconversion. *Mild Preparative Conditions for Conversion of Amines into Pyridinium Ions. Angew. Chem., Int. Ed. Engl* 1980, 19 (4), 306–306.
- (25) (a). Chakraborty S; Newkome GR Terpyridine-Based Metallosupramolecular Constructs: Tailored Monomers to Precise 2D- Motifs and 3D-Metallocages. *Chem. Soc. Rev* 2018, 47 (11), 3991–4016. [PubMed: 29594272] (b)Xie T-Z; Endres KJ; Guo Z; Ludlow JM; Moorefield CN; Saunders MJ; Wesdemiotis C; Newkome GR Controlled Interconversion of Superposed-Bistriangle, Octahedron, and Cuboctahedron Cages Constructed Using a Single, Terpyridinyl-Based Polyligand and Zn^{2+} . *J. Am. Chem. Soc* 2016, 138 (38), 12344–12347. [PubMed: 27610709]
- (26) (a). Brouck ER; Anderson SE; Northrop BH; Stang PJ; Bowers MT Structures of Metallosupramolecular Coordination Assemblies Can Be Obtained by Ion Mobility Spectrometry–Mass Spectrometry. *J. Am. Chem. Soc* 2010, 132 (38), 13486–13494. [PubMed:

- 20815390] (b) Li X; Chan Y-T; Newkome GR; Wesdemiotis C Gradient Tandem Mass Spectrometry Interfaced with Ion Mobility Separation for the Characterization of Supramolecular Architectures. *Anal. Chem* 2011, 83 (4), 1284–1290. [PubMed: 21261266] (c) Thalassinos K; Grabenauer M; Slade SE; Hilton GR; Bowers MT; Scrivens JH Characterization of Phosphorylated Peptides Using Traveling Wave-Based and Drift Cell Ion Mobility Mass Spectrometry. *Anal. Chem* 2009, 81 (1), 248–254. [PubMed: 19117454]
- (27). Sun B; Wang M; Lou Z; Huang M; Xu C; Li X; Chen L-J; Yu Y; Davis GL; Xu B; Yang H-B; Li X From Ring-in-Ring to Sphere-in-Sphere: Self-Assembly of Discrete 2D and 3D Architectures with Increasing Stability. *J. Am. Chem. Soc* 2015, 137 (4), 1556–1564. [PubMed: 25574776]
- (28). Wang J-L; Li X; Lu X; Hsieh IF; Cao Y; Moorefield CN; Wesdemiotis C; Cheng SZD; Newkome GR Stoichiometric Self-Assembly of Shape-Persistent 2D Complexes: A Facile Route to a Symmetric Supramacromolecular Spoked Wheel. *J. Am. Chem. Soc* 2011, 133 (30), 11450–11453. [PubMed: 21657251]
- (29) (a). Giuseppone N; Schmitt J-L; Allouche L; Lehn J-M DOSY NMR Experiments as a Tool for the Analysis of Constitutional and Motional Dynamic Processes: Implementation for the Driven Evolution of Dynamic Combinatorial Libraries of Helical Strands. *Angew. Chem., Int. Ed* 2008, 47 (12), 2235–2239. (b) Schulze BM; Watkins DL; Zhang J; Ghiviriga I; Castellano RK Estimating the Shape and Size of Supramolecular Assemblies by variable Temperature Diffusion Ordered Spectroscopy. *Org. Biomol. Chem* 2014, 12 (40), 7932–7936. [PubMed: 25188902]
- (30). Lu X; Li X; Cao Y; Schultz A; Wang J-L; Moorefield CN; Wesdemiotis C; Cheng SZD; Newkome GR Self-Assembly of a Supramolecular, Three-Dimensional, Spoked, Bicycle-like Wheel. *Angew. Chem., Int. Ed* 2013, 52 (30), 7728–7731.

Figure 1.

(a) Full ESI-MS spectrum with theoretical and experimental isotope patterns of 15+ species (right inset). (b) TWIM-MS (m/z vs drift time) of **KC** composed by three-component *in situ* self-assembly strategy.

Figure 2.
One-pot synthesis of **KC** at 110 °C monitored via ESI-MS at various reaction times.

Figure 3.

(a) Full ESI-MS spectrum with theoretical and experimental isotope patterns of 15+ species (right inset). (b) TWIM-MS (m/z vs drift time) of **SW-1** composed by four-component *in situ* self-assembly strategy.

Figure 4.
 ^1H NMR spectra (600 MHz, d_6 -DMSO, 300 K) of (a) SW-1 and (b) SW-3.

Figure 5.

(a) Full ESI-MS spectrum with theoretical and experimental isotope patterns of 15+ species (right inset). (b) TWIM-MS (m/z vs drift time) of **SW-2** composed by four-component *in situ* self-assembly strategy.

Figure 6.

(a) STM image of individual **SW-1** on Ag(111) surface; (b) zoomed-in STM image of one **SW-1** supramolecule in (a); (d) STM image of individual **SW-2** on Ag(111) surface; (e) zoomed-in STM image of one **SW-2** supramolecule in (d); (c and f) representative energy-minimized structures from molecular modeling of **SW-1** and **SW-2**; alkyl chains were omitted for clarity. Dashed lines covered on the images of (b) and (e) represent the organic backbone of the complexes, pink ovals represent the double-layers of $\langle \text{tpy-Zn(II)-tpy} \rangle$ junctions on the outer rim, and blue/green circles correspond to the $\langle \text{tpy-Zn(II)-tpy} \rangle$ junction linked to the core.

Scheme 1. Preparation of KC^a

^a (a) Conventional self-assembly using presynthesized ligand **L1**; condition: $\text{CHCl}_3/\text{MeOH}$ (1/3, v/v), 50 °C, 3 h. (b) One-pot approach with synthesis and self-assembly together using precursors **A** and **B**; condition: DMSO, 110 °C, 24 h. (c) Synthesis of **L1** from **A** and **B**, condition: DMSO, 120 °C, 24 h.

Scheme 2. Preparation of (a) SW-1 and (b) SW-2 through Four-Component Synthesis/Self-Assembly in One Pot^a

^aCondition: DMSO, 110 °C, 24 h.

Scheme 3. (a) Selective Assembly of SW-1 through the Synthesis/Self-Assembly in One-Pot Strategy Involving Two Core Ligands D and E; and (b) Transforming SW-2 to SW-1 by Adding Equal Equivalency of D^a

^aReaction condition: DMSO, 110 °C, 24 h.