

Hexagon Wreaths: Self-Assembly of Discrete Supramolecular Fractal Architectures Using Multitopic Terpyridine Ligands

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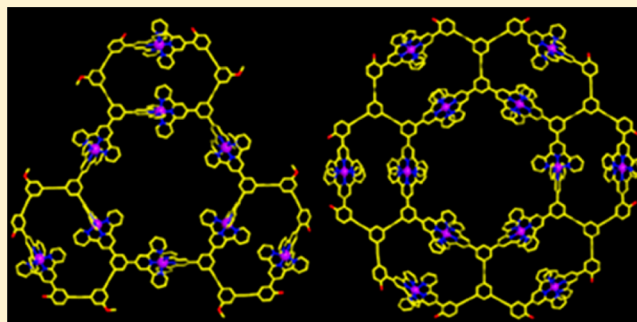
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S Supporting Information

ABSTRACT: In this study, we overcame a challenge in conventional self-assembly of macrocycles that uses ditopic 2,2':6',2''-terpyridine (tpy) building blocks with a 120° angle between two ligating moieties, which generally produces a mixture of multiple macrocycles instead of a single hexagon. Two supramolecular hexagon wreaths, [Zn₉LA₆] and [Zn₁₂LB₆], were designed and self-assembled from tritopic and tetratopic tpy ligands with Zn(II) ions, respectively. These multitopic ligands, bearing multiple binding sites, increased the total density of coordination sites and provided high geometric constraints to induce the formation of discrete structures. Such hexagon wreaths, which were constructed by simple recursion of small hexagons around a central hexagon, exhibit fractal geometry features with self-similarity at different levels. The shapes, sizes, and structures were fully characterized by NMR, ESI-MS, traveling-wave ion mobility mass spectrometry (TWIM-MS), and transmission electron microscopy. With diameters around 5.5 nm for [Zn₉LA₆] and 5.8 nm for [Zn₁₂LB₆], the remarkable rigidity of these fractal architectures was supported by TWIM-MS, in contrast to the high flexibility of macrocycles assembled by ditopic tpy ligands.



INTRODUCTION

Precise control over the shape and size of supramolecular architectures through self-assembly has been a major driving force for chemists over the past few decades.^{1,2} As supramolecular chemistry has become a highly diverse field, metallo-macrocycles have been marked by the successful construction of a wide array of two-dimensional (2D) geometries with increasing complexity since the seminal work of Stang et al.³ and Fujita et al.,⁴ including triangles,⁵ squares,⁶ rectangles,⁷ rhomboids,⁸ pentagons,⁹ hexagons,¹⁰ and large ring systems.¹¹ Such well-defined structures with high diversity and complexity make metallo-macrocycles an ideal platform for scientists seeking to design novel materials with molecular-level precision.^{1c,h,12} Among the possible applications, metallo-macrocycles are being investigated as new materials in a variety of contexts with excellent sensing,¹³ magnetic,¹⁴ photonic,¹⁵ enantiomeric enrichment,¹⁶ and catalytic properties.¹⁷

In many cases, the success of such assemblies with precise shapes and sizes mainly relies on the angles of the organic ligands and the coordination geometry of the metal ions.^{1a,b}

The weak bonding strength of metal–ligand interactions helps in modulating the coordination kinetics of self-assembly processes by introducing rigidity and reversibility. However, unpredicted macrocycles often appear because organic ligands are much more flexible than expected and metal centers can allow considerable deviation in their coordination geometry. Therefore, assemblies with similar components resulting in an equilibrating mixture of binary or multiple entities instead of single discrete structures have been reported. Using binary systems as an example, Stang,¹⁸ Fujita,¹⁹ Schalley,²⁰ and others²¹ reported cases of triangle–square equilibria with Pd(II)- and Pt(II)-based self-assembly. In a study of multiple entities, Lin and co-workers used stepwise directed assembly to obtain a family of macrocycles with kinetically inert Pt–alkynyl linkages^{11d,22} from a supramolecular library.^{11e}

Moving to the self-assembly of 2,2':6',2''-terpyridine (tpy),²³ which has attracted considerable attention in supramolecular

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polymers,²⁴ 2D macrocycles,^{10b,25} three-dimensional (3D) cages,²⁶ and heteroleptic coordination-based self-assembly,²⁷ Newkome and co-workers recently succeeded in isolating unexpected pentameric, heptameric, octameric, nonameric, and decameric macrocycles composed of rigid ditopic tpy ligands with 120° orientation of their metal binding sites.²⁸ Nevertheless, precise control over the self-assembly of metallo-macrocycles toward discrete structures is still one of the ultimate goals and challenges in the field of supramolecules, recalling that many weak (noncovalent) interactions, acting cooperatively, can yield stable supramolecular complexes.²⁹ For example, intramolecular noncovalent interactions are largely responsible for the stable secondary and tertiary structures of proteins and therefore the proteins' functions in the mechanisms of life.³⁰ Therefore, we reason that a system with a high density of noncovalent interactions is preferable to form a discrete architecture. Accordingly, we herein designed two hexagon wreath structures (Figure 1) assembled by tritopic (LA, Scheme 1A) and tetratopic tpy ligands (LB, Scheme 2A). Compared to ditopic ligands used in the self-assembly of conventional macrocycles, our strategy increased the number of coordination sites within the hexagon wreath, which was named the “density of coordination sites” (DOCS), and thus provided more constraints to form discrete and thermodynamically stable structures. Remarkably, such hexagon wreaths, which were constructed by simple recursion of small hexagons around the center hexagon, exhibit fractal geometry features with self-similarity at different levels.³¹

RESULTS AND DISCUSSION

A Sonogashira coupling reaction was used to synthesize ligand LA (Scheme 1A) in a decent yield, purified by column chromatography (Al_2O_3). LA and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed in a stoichiometric ratio (2:3) in $\text{CHCl}_3/\text{MeOH}$ at 55 °C for 12 h, followed by addition of an excess of NH_4PF_6 salt to give a white precipitate (complex $[\text{Zn}_9\text{LA}_6]$, yield 88%) with nine coordination sites.

The ^1H NMR spectrum of complex $[\text{Zn}_9\text{LA}_6]$ is shown in Figure 2. There are 24 sets of aromatic protons from three sets of tpy units and phenyl groups in the aromatic region of $[\text{Zn}_9\text{LA}_6]$; only two sets of tpy units were found in the ^1H NMR spectrum of LA. Many proton signals of the pyridine rings are overlapping in the ^1H NMR spectrum of complex $[\text{Zn}_9\text{LA}_6]$. According to 2D-COSY results (Figures S23–S25), there are three groups of ^1H signals from tpy, as expected. Furthermore, the NMR spectrum of $[\text{Zn}_9\text{LA}_6]$ shows broad ^1H signals, due to its slow tumbling motion on the NMR time scale,³² suggesting a very large complex was obtained. We also performed temperature-dependent NMR studies from 28 to 70 °C for $[\text{Zn}_9\text{LA}_6]$.³³ NMR signals became slightly sharper with splitting between 50 and 70 °C rather than showing a significant improvement (see Figure S27). However, this complex could not tolerate temperatures higher than 70 °C and immediately decomposed into an unassignable mixture of oligomers because of the labile nature of the Zn(II)–terpyridine coordination (data not shown). Because electron density was lower upon coordination with metal ions, both the 3',5'-tpy and a3',a5'-tpy protons were significantly shifted downfield. For this complexation with Zn(II), all the 6-position signals of pyridine shifted upfield ($\Delta\delta = 0.8$ ppm) due to the electron shielding effect.^{25b} At the same time, almost all other aromatic proton signals were shifted to downfield. There is only one set of proton signals for methoxy ($-\text{OCH}_3$) and alkyloxy

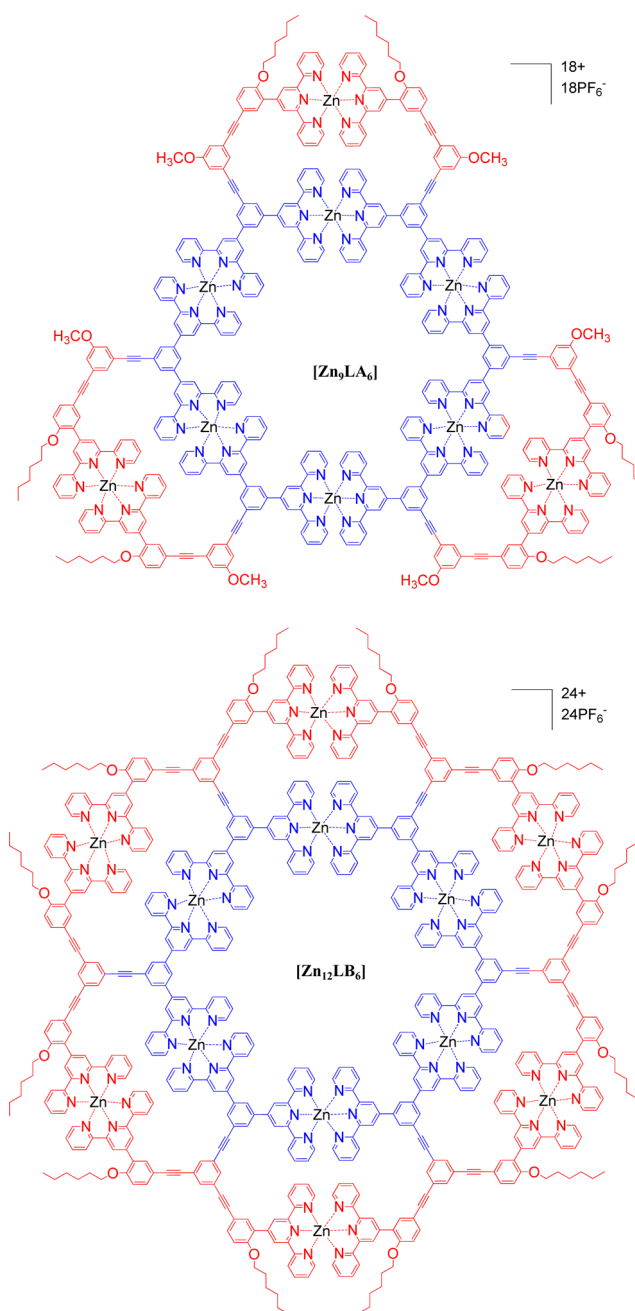
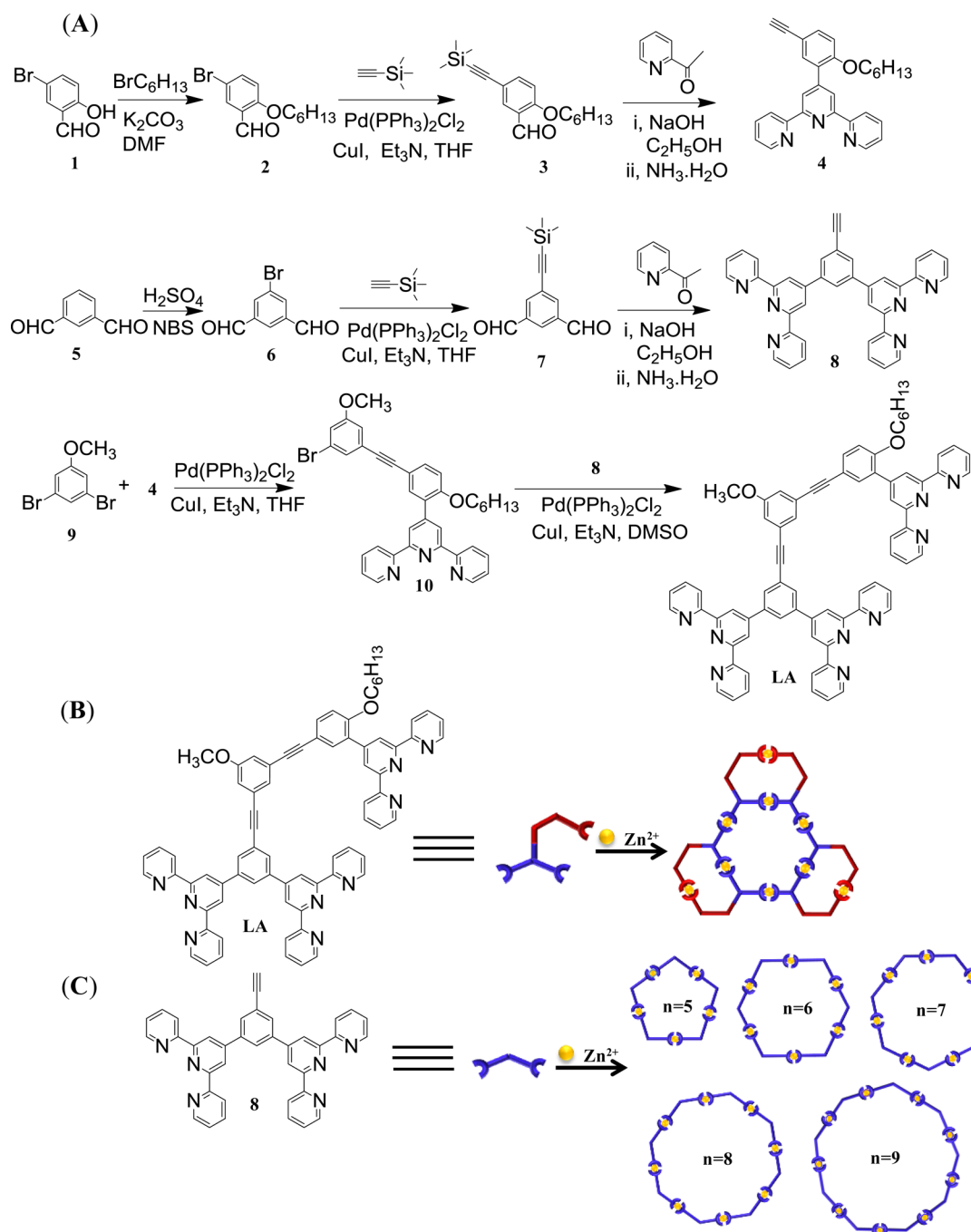


Figure 1. Structures of hexagon wreaths $[\text{Zn}_9\text{LA}_6]$ and $[\text{Zn}_{12}\text{LB}_6]$.

chains ($-\text{OCH}_2-$), suggesting the possibility of a single component in the product.

Electrospray ionization mass spectrometry (ESI-MS) and traveling-wave ion mobility mass spectrometry (TWIM-MS) have been recognized as effective methods to determine molecular composition and provide shape and size information.^{28c,34} In Figure 3A, only one prominent set of peaks with different charge states (7+ to 12+) is observed (due to the loss of a different number of PF_6^-). Each isotope pattern of these peaks agrees excellently with the corresponding simulated isotope pattern of $[\text{Zn}_9\text{LA}_6]$ (Figure S1) for the desired hexagon wreath structure with molecular weight of 9793.4 Da. This complex was further characterized by TWIM-MS to separate any superimposed fragments and detect the possible presence of overlapping isomers or conformers. As a variant of conventional ion mobility MS,³⁵ TWIM-MS has been used as a

Scheme 1. (A) Synthetic Route to Ligand LA, (B) Self-Assembly of Discrete Hexagon Wreath $[\text{Zn}_9\text{LA}_6]$, and (C) Self-Assembly of Multiple Macrocycles ($n = 5-9$) by Ligand 8

powerful method to determine the ion's mass, charge, and shape via the drift time.^{25,34,35} As the TWIM-MS result shows in Figure 3B, each charge state is detected with a narrow drift time distribution, indicating this complex is a single-component product without other isomers or structural conformers. Compared to macrocycles assembled by 120° ditopic tpy ligands, multiple isomers and conformers were observed in TWIM-MS.²⁸

In sharp contrast with the discrete hexagon wreath, self-assembly of ditopic tpy compound 8 (Scheme 1) with $\text{Zn}(\text{II})$ under the same conditions was observed as a mixture of multiple macrocycles by ESI-MS, including pentamer to nonamer (Figure 4). This is consistent with the previous self-

assembly study of ditopic tpy ligand with a 120° geometry between metal binding sites.²⁸ After three small hexagons were introduced around the core hexagon, the self-assembly gave a single structure of $[\text{Zn}_9\text{LA}_6]$ instead of multiple macrocycles. Therefore, we postulated that the self-assembly of discrete hexagon wreath $[\text{Zn}_9\text{LA}_6]$ was induced by these three small hexagons around the outer rim. Such small hexagons possessing a higher density of coordination sites provides the whole supramolecular fractal with greater rigidity and geometric constraints, forcing the internal ditopic moieties with 120° angle into a single hexagon wreath structure.

In order to prove this assumption, we performed another self-assembly using ligand LA with $\text{Zn}(\text{II})$ at a molar ratio of

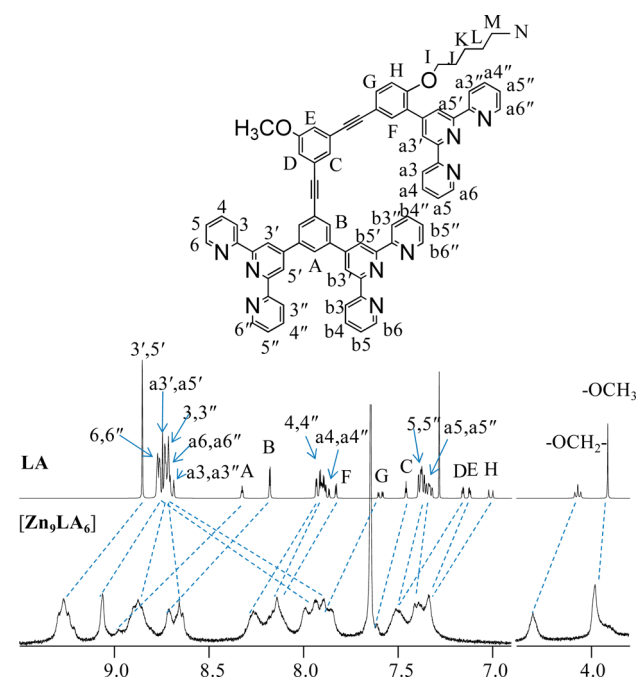


Figure 2. ^1H NMR spectra (400 MHz) of ligand **LA** in CDCl_3 and complex $[\text{Zn}_9\text{LA}_6]$ in CD_3CN .

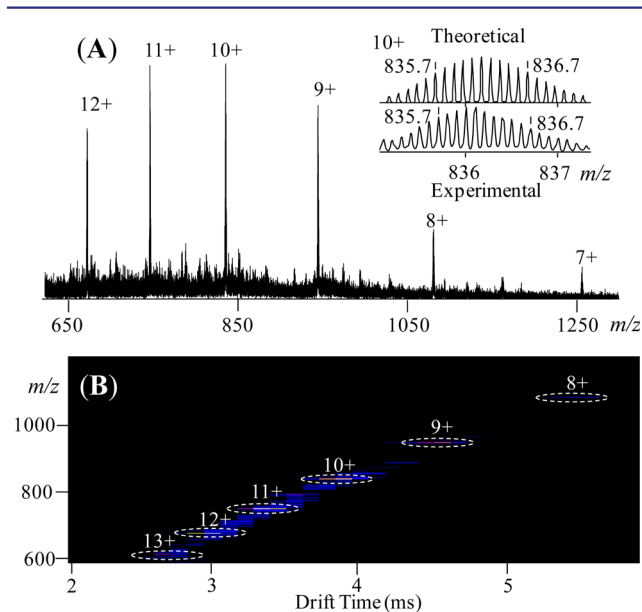


Figure 3. (A) ESI-MS and (B) 2D ESI-TWIM-MS plot (m/z vs drift time) of hexagon wreath $[\text{Zn}_9\text{LA}_6]$. The charge states of intact assemblies are marked.

1:1. According to the structure of ligand **LA**, if the ratio of ligand and metal is 1:1, we should observe the formation of a small hexagon-like dimer as a preferable structure with two **LA** and two metals under entropy-driven conditions. As shown in Figure 5, one main set of peaks at different charge states ($Z = 2+$ to $4+$) is observed in ESI-MS, corresponding to the dimer structure. The knowledge gained in this initial study inspired us to design more-sophisticated structures by applying the small hexagon-like dimer to induce the formation of discrete architectures. Here this small dimer was utilized as the basic subunit in the recursion process toward large fractal geometry.

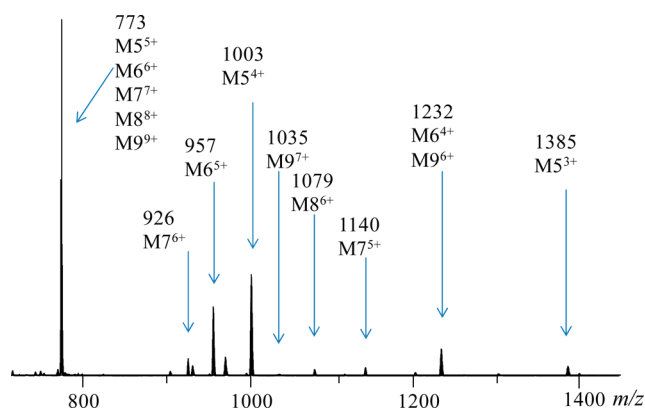


Figure 4. ESI-MS of multiple macrocycles assembled by ditopic tpy ligand **8** with $\text{Zn}(\text{II})$. The m/z ratio and possible ion compositions are marked above the peaks. Macrocycle complexes are named Mn^{x+} , where M designates the repeat unit $\langle \text{tpy-Zn-tpy} \rangle$, n is the number of repeat units, and x is the number of charges.

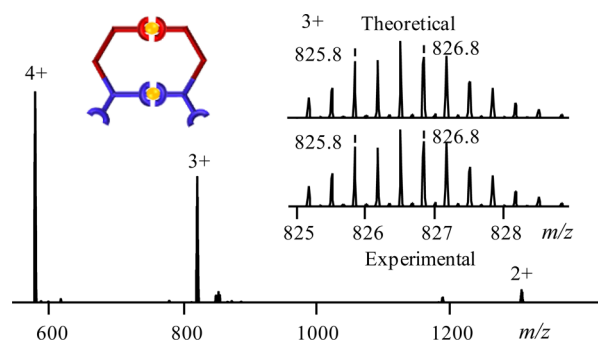


Figure 5. ESI-MS and isotope pattern of the hexagon-like dimer obtained by self-assembly of **LA** with $\text{Zn}(\text{II})$ at a molar ratio of 1:1.

Following this result, a tetratopic ligand **LB** was designed and synthesized to build a more-complicated hexagon wreath, $[\text{Zn}_{12}\text{LB}_6]$ (Figure 1), which possesses six small hexagons around a central hexagon. In this fractal architecture, the self-similarity was realized by a simple recursion of small hexagons around a central hexagon. The synthetic route to ligand **LB** is shown in Scheme 2A. Long alkyl chains were incorporated around the outer rim of the hexagon wreath to increase the solubility of complex $[\text{Zn}_{12}\text{LB}_6]$.

Furthermore, the highly symmetric structure of **LB** simplified the ^1H NMR spectra and facilitated characterization. Complex $[\text{Zn}_{12}\text{LB}_6]$ was successfully obtained in 91% yield by using the same self-assembly procedure as for $[\text{Zn}_9\text{LA}_6]$. Compared to the three sets of tpy signals in $[\text{Zn}_9\text{LA}_6]$, the ^1H NMR spectrum of $[\text{Zn}_{12}\text{LB}_6]$ shows only two sets of tpy signals, indicating the formation of a highly symmetric architecture (Figure 6). Except for the 6-position of pyridine, which was shifted upfield ($\Delta\delta = 0.75$ ppm), all other aromatic proton peaks (tpy and phenyl) were shifted slightly downfield. Note that the full assignments of the ^1H NMR spectra shown in Figure 6 were based on 2D-COSY (see Figures S30–S32). 2D NOESY and HSQC NMR are also consistent with this hexagon wreath as the sole product (see Figures S33 and S34). Temperature-dependent NMR analysis of complex $[\text{Zn}_{12}\text{LB}_6]$ was also performed, as for $[\text{Zn}_9\text{LA}_6]$, showing a slight improvement between 50 and 70 $^\circ\text{C}$ (Figure S35).

The ESI result of this complex is depicted in Figure 7A. Different charge states of the complex ($Z = 10+$ to $19+$) were

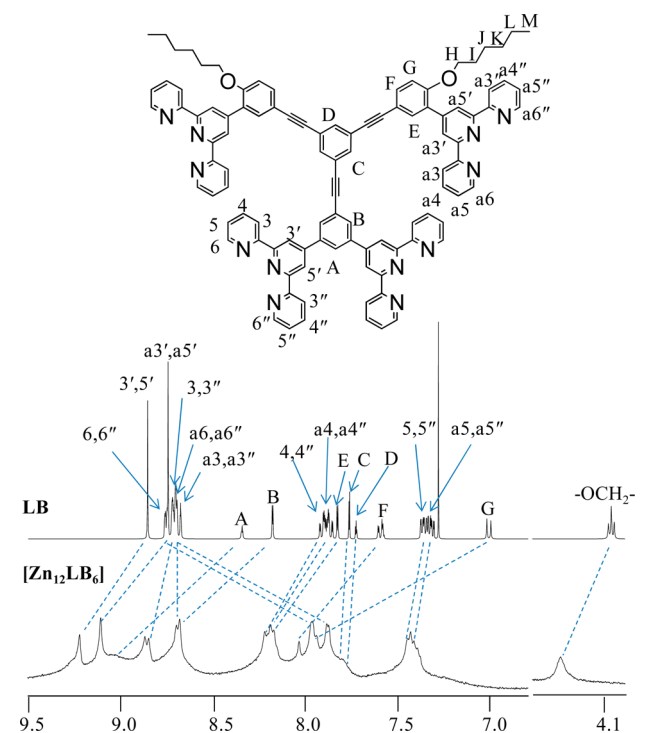
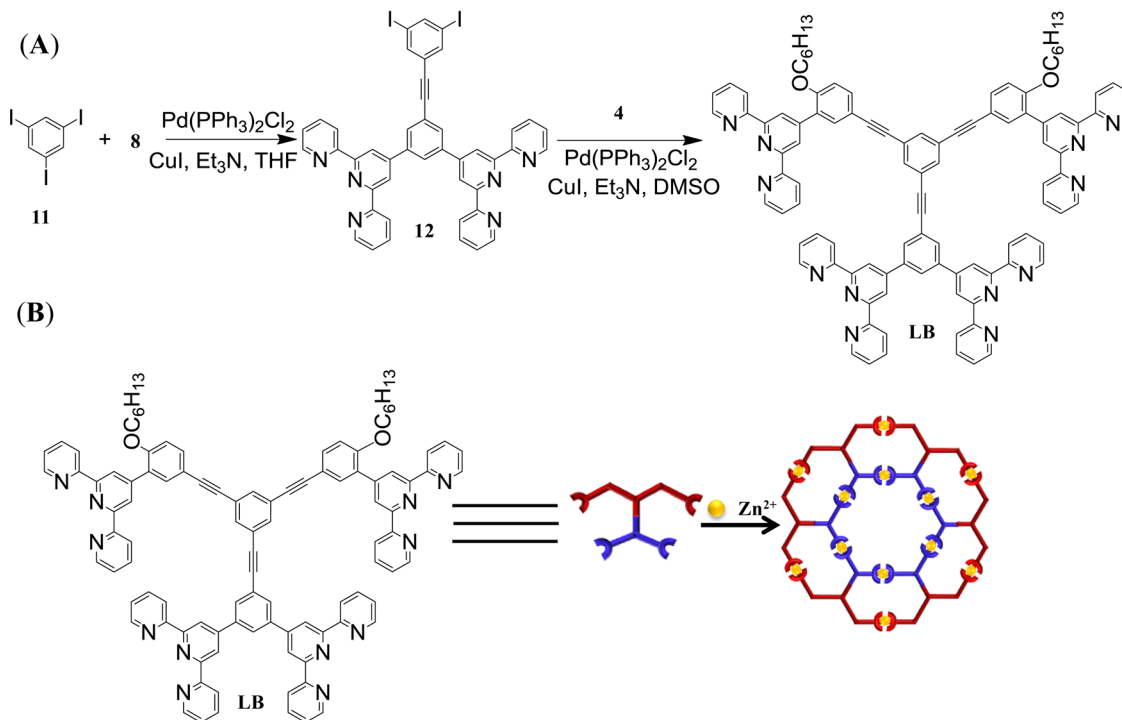
Scheme 2. (A) Synthetic Route to Ligand LB and (B) Self-Assembly of Discrete Hexagon Wreath $[\text{Zn}_{12}\text{LB}_6]$ 

Figure 6. ^1H NMR spectra (400 MHz) of ligand LB in CDCl_3 and complex $[\text{Zn}_{12}\text{LB}_6]$ in CD_3CN .

observed, and the corresponding isotope patterns are shown in Figure S3. The molecular weight of this giant hexagon wreath was measured as 13 262.1 Da. With further characterization by TWIM-MS (Figure 7B), the narrow distribution of each charge state confirms that no isomer or conformer was generated in the self-assembly. It suggests the formation of the hexagon wreath as a single, rigid structure. The self-assembly of such

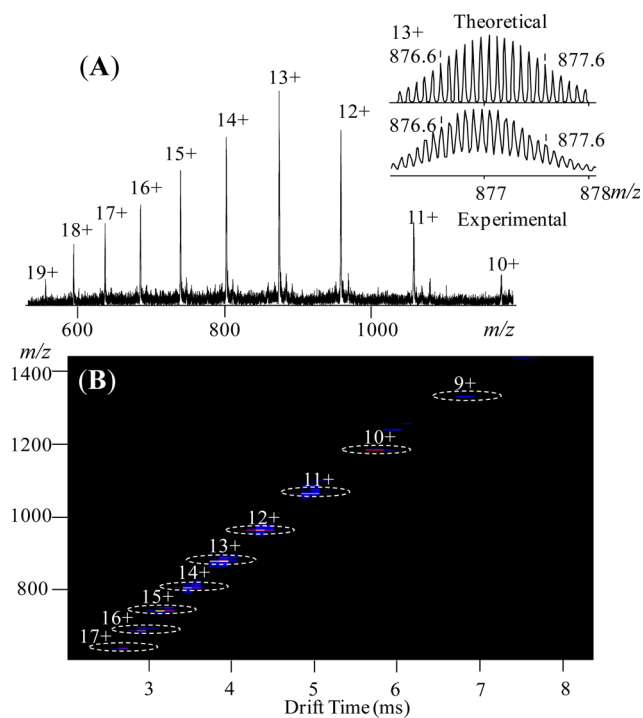


Figure 7. (A) ESI-MS and (B) 2D ESI-TWIM-MS plot (m/z vs drift time) of hexagon wreath $[\text{Zn}_{12}\text{LB}_6]$. The charge states of intact assemblies are marked.

discrete complexes indicates that increasing the density of coordination sites by applying multitopic ligands is a feasible approach toward single discrete structures instead of multiple entities by ditopic build blocks.

To gain more information about the sizes and shapes of these two complexes, collision cross sections (CCSs), which correspond to the sizes of analytes, can be employed to

provide further evidence.^{34,35} Experimental CCSs of the ions were derived from the drift time of TWIM-MS data using standard curves.³⁶ Theoretical CCSs, which were calculated from molecular modeling, were correlated with experimental CCSs deduced for these two hexagon wreath complexes at various charge states (Table 1). The trajectory (TJ), projection

Table 1. Experimental and Theoretical Collision Cross Sections (\AA^2)

drift time (ms)	CCS	average CCS	calcd avg CCS
[Zn ₉ LA ₆]			
6.62 (7+)	1463.5		
5.29 (8+)	1457.3		
4.41 (9+)	1463.2		1472.2 ± 74.4 ^b
3.75 (10+)	1467.3	1478.4(23.6) ^a	1272.8 ± 67.4 ^c
3.31 (11+)	1490.4		1542.8 ± 76.3 ^d
2.87 (12+)	1482.4		
2.65 (13+)	1524.8		
[Zn ₁₂ LB ₆]			
6.62 (9+)	1880.3		
5.62 (10+)	1890.0		
4.74 (11+)	1869.5		
4.19 (12+)	1887.3		1946.7 ± 40.7 ^b
3.75 (13+)	1905.9	1898.4(21.1) ^a	1657.1 ± 25.1 ^c
3.31 (14+)	1894.8		2038.9 ± 29.9 ^d
2.98 (15+)	1896.8		
2.76 (16+)	1924.8		
2.54 (17+)	1936.5		

^aAverage of all CCS values. ^bTrajectory (TJ) value obtained using MOBCAL. ^cProjection approximation (PA) value obtained using MOBCAL. ^dExact hard-sphere scattering (EHSS) value obtained using MOBCAL.

approximation (PA), and exact hard-sphere scattering (EHSS) method were applied to calculate average theoretical CCSs for 70 candidate structures of [Zn₉LA₆] and [Zn₁₂LB₆] from annealing using MOBCAL.³⁷ The plots of relative energy and CCSs are shown in Figures S4–S9. Note that these 70 candidate structures were weighted equally in their contribution to the average theoretical CCS. As a result, the TJ method closely matched the average experimental CCS results for different charge states in these three methods (Table 1), because the TJ method considers both long-range interactions and momentum transfer between the ions and the gas in the ion mobility region.³⁷ As shown in Table 1, the experimental CCS of [Zn₉LA₆] is 1478.4 ± 23.6 \AA^2 , in excellent agreement with the theoretical CCS, i.e., 1472.2 ± 74.4 \AA^2 by TJ. The experimental and theoretical CCSs of [Zn₉LA₆] were also found to be in good agreement, i.e., 1898.4 ± 21.1 \AA^2 vs 1946.7 ± 40.7 \AA^2 . The slight difference in the CCSs at each charge state quantitatively suggests the remarkable rigidity of these species is due to their high geometric constraints from a high density of coordination sites; in contrast, the CCSs of macrocycles assembled from ditopic ligands were vastly different at different charge states due to their high flexibility.²⁸

Finally, the sizes and shapes of individual molecules for these two hexagon wreath structures were characterized by transmission electron microscopy (TEM) on a JEOL 2010 microscope (Figures 8 and S36). The sizes observed by TEM were consistent with theoretical ones calculated from molecular simulation using Materials Studio (5.5 nm for [Zn₉LA₆] and

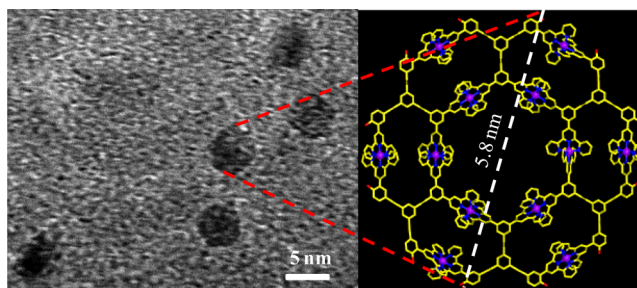


Figure 8. TEM image (left) and energy-minimized structures from molecular modeling (right) of complex [Zn₁₂LB₆]. The long alkyl chains are omitted for clarity in the molecular modeling.

5.8 nm for [Zn₁₂LB₆]). Besides the structural characterization, the ultraviolet absorption and fluorescence spectra of the two ligands and their complexes were also evaluated, showing similar results (see Figure S10).

CONCLUSIONS

Instead of using ditopic building blocks in conventional self-assembly of macrocycles, we employed multitopic terpyridine ligands to precisely control the size and shape of 2D self-assembly. These multitopic ligands provided more noncovalent interactions and significantly increased the density of coordination sites within 2D structures, thus inducing the self-assembly of discrete architectures. In other words, the high density of coordination generated more geometric constraints to prevent the formation of multiple entities. Two hexagon wreath structures with fractal features were designed by introducing three and six small hexagons around the center hexagon, respectively. The strategy used in this study will not only refresh the interest in self-assembly of macrocycles but also advance the design of more sophisticated 2D architectures. Recall that fractal geometry is a recursive mathematical derivation of a form that possesses self-similar structures at various levels of scale or detail. The success of these two discrete supramolecular fractals opens a new avenue facilitating the construction of complicated fractal geometry with self-similarity by a simple recursion process.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Lehn, J.-M. *Chem. Soc. Rev.* **2007**, *36*, 151. (d) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161. (e) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (f) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. *Coord. Chem. Rev.* **2008**, *252*, 825. (g) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (h) Wurthner, F.; You, C.-C.; Saha-Moller, C. R. *Chem. Soc. Rev.* **2004**, *33*, 133. (i) Nitschke, J. R. *Acc. Chem. Res.* **2007**, *40*, 103. (j) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521. (k) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434.
- (2) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (b) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488. (c) Saalfrank, R. W.; Maid, H.; Scheurer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8794.
- (3) (a) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (b) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (c) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.
- (4) (a) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645. (b) Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (c) Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720. (d) Fujita, M.; Ibukuro, F.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 4175.
- (5) (a) Rasika Dias, H. V.; Palehepitiya Gamage, C. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2192. (b) Schnebeck, R.-D.; Freisinger, E.; Glahé, F.; Lippert, B. *J. Am. Chem. Soc.* **2000**, *122*, 1381. (c) Hwang, S.-H.; Moorefield, C. N.; Fronczek, F. R.; Lukoyanova, O.; Echegoyen, L.; Newkome, G. R. *Chem. Commun.* **2005**, 713. (d) Kryschenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 5193. (e) Schmittel, M.; Mahata, K. *Chem. Commun.* **2008**, 2550. (f) Schmittel, M.; Mahata, K. *Inorg. Chem.* **2009**, *48*, 822. (g) Mahata, K.; Saha, M. L.; Schmittel, M. *J. Am. Chem. Soc.* **2010**, *132*, 15933.
- (6) (a) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524. (b) Stang, P. J.; Cao, D. H.; Chen, K.; Gray, G. M.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5163. (c) You, C.-C.; Würthner, F. *J. Am. Chem. Soc.* **2003**, *125*, 9716. (d) Sautter, A.; Kaletas, B. K.; Schmid, D. G.; Dobrawa, R.; Zimine, M.; Jung, G.; van Stokkum, I. H. M.; De Cola, L.; Williams, R. M.; Würthner, F. *J. Am. Chem. Soc.* **2005**, *127*, 6719.
- (7) Saha, M. L.; Schmittel, M. *J. Am. Chem. Soc.* **2013**, *135*, 17743.
- (8) (a) Yang, H.-B.; Das, N.; Huang, F.; Hawkrige, A. M.; Díaz, D. D.; Arif, A. M.; Finn, M. G.; Muddiman, D. C.; Stang, P. J. *J. Org. Chem.* **2006**, *71*, 6644. (b) Lu, J.; Turner, D. R.; Harding, L. P.; Byrne, L. T.; Baker, M. V.; Batten, S. R. *J. Am. Chem. Soc.* **2009**, *131*, 10372. (c) Lu, X.; Li, X.; Wang, J.-L.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Commun.* **2012**, *48*, 9873.
- (9) (a) Zhao, L.; Ghosh, K.; Zheng, Y.; Lyndon, M. M.; Williams, T. I.; Stang, P. J. *Inorg. Chem.* **2009**, *48*, 5590. (b) Campos-Fernández, C. S.; Schottel, B. L.; Chifotides, H. T.; Bera, J. K.; Bacsa, J.; Koomen, J. M.; Russell, D. H.; Dunbar, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 12909. (c) Hwang, S.-H.; Wang, P.; Moorefield, C. N.; Godinez, L. A.; Manriquez, J.; Bustos, E.; Newkome, G. R. *Chem. Commun.* **2005**, 4672.
- (10) (a) Stang, P. J.; Persky, N. E.; Manna, J. *J. Am. Chem. Soc.* **1997**, *119*, 4777. (b) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Baker, G. R.; Cush, R.; Russo, P. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3717. (c) Wang, G.-L.; Lin, Y.-J.; Jin, G.-X. *Chem.—Eur. J.* **2011**, *17*, 5578.
- (11) (a) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed.* **1996**, *35*, 1838. (b) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956. (c) Newkome, G. R.; Wang, P.; Moorefield, C. N.; Cho, T. J.; Mohapatra, P. P.; Li, S.; Hwang, S.-H.; Lukoyanova, O.; Echegoyen, L.; Palagallo, J. A.; Iancu, V.; Hla, S.-W. *Science* **2006**, *312*, 1782. (d) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2004**, *126*, 7426. (e) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 8084.
- (12) Lehn, J.-M. *Science* **2002**, *295*, 2400.
- (13) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554.
- (14) (a) Kahn, O. *Acc. Chem. Res.* **2000**, *33*, 647. (b) Dul, M.-C.; Pardo, E.; Lescouëzec, R.; Journaux, Y.; Ferrando-Soria, J.; Ruiz-García, R.; Cano, J.; Julve, M.; Lloret, F.; Cangussu, D.; Pereira, C. L. M.; Stumpf, H. O.; Pasán, J.; Ruiz-Pérez, C. *Coord. Chem. Rev.* **2010**, *254*, 2281.
- (15) (a) Flynn, D. C.; Ramakrishna, G.; Yang, H.-B.; Northrop, B. H.; Stang, P. J.; Goodson, T. *J. Am. Chem. Soc.* **2010**, *132*, 1348. (b) Pollock, J. B.; Schneider, G. L.; Cook, T. R.; Davies, A. S.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 13676.
- (16) (a) Yeh, R. M.; Raymond, K. N. *Inorg. Chem.* **2006**, *45*, 1130. (b) Gregoliński, J.; Starynowicz, P.; Hua, K. T.; Lunkley, J. L.; Muller, G.; Lisowski, J. *J. Am. Chem. Soc.* **2008**, *130*, 17761. (c) Heo, J.; Jeon, Y.-M.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 7712.
- (17) (a) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948. (b) Huang, S.-L.; Lin, Y.-J.; Hor, T. S. A.; Jin, G.-X. *J. Am. Chem. Soc.* **2013**, *135*, 8125. (c) Gadzikwa, T.; Bellini, R.; Dekker, H. L.; Reek, J. N. H. *J. Am. Chem. Soc.* **2012**, *134*, 2860.
- (18) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Inorg. Chem.* **2002**, *41*, 2556.
- (19) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535.
- (20) Weilandt, T.; Troff, R. W.; Saxell, H.; Rissanen, K.; Schalley, C. A. *Inorg. Chem.* **2008**, *47*, 7588.
- (21) (a) Lee, S. B.; Hwang, S.; Chung, D. S.; Yun, H.; Hong, J.-I. *Tetrahedron Lett.* **1998**, *39*, 873. (b) Sautter, A.; Schmid, D. G.; Jung, G.; Würthner, F. *J. Am. Chem. Soc.* **2001**, *123*, 5424. (c) Zhang, L.; Niu, Y.-H.; Jen, A. K.-Y.; Lin, W. *Chem. Commun.* **2005**, 1002. (d) Uehara, K.; Kasai, K.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 2563. (e) Uehara, K.; Kasai, K.; Mizuno, N. *Inorg. Chem.* **2010**, *49*, 2008.
- (22) Jiang, H.; Lin, W. *J. Am. Chem. Soc.* **2006**, *128*, 11286.
- (23) (a) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (b) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373. (c) Wild, A.; Winter, A.; Schlutter, F.; Schubert, U. S. *Chem. Soc. Rev.* **2011**, *40*, 1459. (d) Constable, E. C. *Coord. Chem. Rev.* **2008**, *252*, 842. (e) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555.
- (24) (a) Whittell, G. R.; Hager, M. D.; Schubert, U. S.; Manners, I. *Nat. Mater.* **2011**, *10*, 176. (b) Mansfeld, U.; Hager, M. D.; Hoogenboom, R.; Ott, C.; Winter, A.; Schubert, U. S. *Chem. Commun.* **2009**, 3386. (c) Mansfeld, U.; Winter, A.; Hager, M. D.; Hoogenboom, R.; Gunther, W.; Schubert, U. S. *Polym. Chem.* **2013**, *4*, 113. (d) Mansfeld, U.; Winter, A.; Hager, M. D.; Festag, G.; Hoepfner, S.; Schubert, U. S. *Polym. Chem.* **2013**, *4*, 3177.
- (25) (a) Chan, Y.-T.; Li, X.; Soler, M.; Wang, J.-L.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2009**, *131*, 16395. (b) Wang, J.-L.; Li, X.; Lu, X.; Hsieh, I. F.; Cao, Y.; Moorefield, C. N.; Wesdemiotis, C.; Cheng, S. Z. D.; Newkome, G. R. *J. Am. Chem. Soc.* **2011**, *133*, 11450. (c) Schultz, A.; Li, X.; Barkakaty, B.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2012**, *134*, 7672.
- (26) (a) Schröder, T.; Brodbeck, R.; Letzel, M. C.; Mix, A.; Schnatwinkel, B.; Tonigold, M.; Volkmer, D.; Mattay, J. *Tetrahedron Lett.* **2008**, *49*, 5939. (b) Wang, C.; Hao, X.-Q.; Wang, M.; Guo, C.; Xu, B.; Tan, E. N.; Zhang, Y.; Yu, Y.; Li, Z.-Y.; Yang, H.-B.; Song, M.-P.; Li, X. *Chem. Sci.* **2014**, *5*, 1221.
- (27) (a) Schmittel, M.; He, B. *Chem. Commun.* **2008**, 4723. (b) Schmittel, M.; He, B.; Mal, P. *Org. Lett.* **2008**, *10*, 2513. (c) Cardona-Serra, S.; Coronado, E.; Gavina, P.; Ponce, J.; Tatay, S. *Chem. Commun.* **2011**, *47*, 8235.
- (28) (a) Chan, Y.-T.; Li, X.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem.—Eur. J.* **2011**, *17*, 7750. (b) Chan, Y.-T.; Li, X.; Yu, J.; Carri, G. A.; Moorefield, C. N.; Newkome, G. R.; Wesdemiotis, C. *J. Am. Chem. Soc.* **2011**, *133*, 11967. (c) Wang, J.-L.; Li, X.; Lu, X.; Chan, Y.-T.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem.—Eur. J.* **2011**, *17*, 4830. (d) Li, X.; Chan, Y.-T.; Casiano-Maldonad, M.; Yu, J.; Carri, G. A.; Newkome, G. R.; Wesdemiotis, C. *Anal. Chem.* **2011**, *83*, 6667.

(29) Fasting, C.; Schalley, C. A.; Weber, M.; Seitz, O.; Hecht, S.; Kokschi, B.; Dervedde, J.; Graf, C.; Knapp, E.-W.; Haag, R. *Angew. Chem., Int. Ed.* **2012**, *51*, 10472.

(30) (a) Breuker, K.; McLafferty, F. W. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18145. (b) Rappas, M.; Schumacher, J.; Beuron, F.; Niwa, H.; Bordes, P.; Wigneshweraraj, S.; Keetch, C. A.; Robinson, C. V.; Buck, M.; Zhang, X. *Science* **2005**, *307*, 1972. (c) Ruotolo, B. T.; Giles, K.; Campuzano, L.; Sandercock, A. M.; Bateman, R. H.; Robinson, C. V. *Science* **2005**, *310*, 1658.

(31) (a) Barnsley, M. F. *Fractals Everywhere*; Morgan Kaufmann Publishers: Burlington, MA, 1993. (b) Mandelbrot, B. *Fractals: form, chance and dimension*; W. H. Freeman and Co.: New York, 1977.

(32) (a) Sun, Q.-F.; Iwasa, J.; Ogawa, D.; Ishido, Y.; Sato, S.; Ozeki, T.; Sei, Y.; Yamaguchi, K.; Fujita, M. *Science* **2010**, *328*, 1144. (b) Sun, Q.-F.; Sato, S.; Fujita, M. *Nat. Chem.* **2012**, *4*, 330. (c) Black, S. P.; Stefankiewicz, A. R.; Smulders, M. M. J.; Sattler, D.; Schalley, C. A.; Nitschke, J. R.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5749. (d) Mahata, K.; Frischmann, P. D.; Würthner, F. *J. Am. Chem. Soc.* **2013**, *135*, 15656.

(33) (a) Saalfrank, R. W.; Maid, H.; Scheurer, A.; Puchta, R.; Bauer, W. *Eur. J. Inorg. Chem.* **2010**, *2010*, 2903. (b) Saalfrank, R. W.; Deutscher, C.; Maid, H.; Ako, A. M.; Sperner, S.; Nakajima, T.; Bauer, W.; Hampel, F.; Heß, B. A.; van Eikema Hommes, N. J. R.; Puchta, R.; Heinemann, F. W. *Chem.—Eur. J.* **2004**, *10*, 1899.

(34) (a) Perera, S.; Li, X.; Soler, M.; Schultz, A.; Wesdemiotis, C.; Moorefield, C. N.; Newkome, G. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6539. (b) Ujma, J.; De Cecco, M.; Chepelin, O.; Levene, H.; Moffat, C.; Pike, S. J.; Lusby, P. J.; Barran, P. E. *Chem. Commun.* **2012**, *48*, 4423. (c) Thiel, J.; Yang, D.; Rosnes, M. H.; Liu, X.; Yvon, C.; Kelly, S. E.; Song, Y.-F.; Long, D.-L.; Cronin, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8871. (d) Scarff, C. A.; Snelling, J. R.; Knust, M. M.; Wilkins, C. L.; Scrivens, J. H. *J. Am. Chem. Soc.* **2012**, *134*, 9193. (e) Ruotolo, B. T.; Benesch, J. L. P.; Sandercock, A. M.; Hyung, S. J.; Robinson, C. V. *Nat. Protoc.* **2008**, *3*, 1139.

(35) (a) Bocker, E. R.; Anderson, S. E.; Northrop, B. H.; Stang, P. J.; Bowers, M. T. *J. Am. Chem. Soc.* **2010**, *132*, 13486. (b) Bowers, M. T.; Kemper, P. R.; von Helden, G.; Koppen, P. A. M. *Science* **1993**, *260*, 1446. (c) Clemmer, D. E.; Jarrold, M. F. *J. Mass Spectrom.* **1997**, *32*, 577. (d) Trimpin, S.; Plasencia, M.; Isailovic, D.; Clemmer, D. E. *Anal. Chem.* **2007**, *79*, 7965. (e) Fenn, L. S.; McLean, J. A. *Anal. Bioanal. Chem.* **2008**, *391*, 905. (f) Silveira, J. A.; Fort, K. L.; Kim, D.; Servage, K. A.; Pierson, N. A.; Clemmer, D. E.; Russell, D. H. *J. Am. Chem. Soc.* **2013**, *135*, 19147.

(36) Thalassinou, K.; Grabenauer, M.; Slade, S. E.; Hilton, G. R.; Bowers, M. T.; Scrivens, J. H. *Anal. Chem.* **2008**, *81*, 248.

(37) (a) Shvartsburg, A. A.; Jarrold, M. F. *Chem. Phys. Lett.* **1996**, *261*, 86. (b) Shvartsburg, A. A.; Liu, B.; Siu, K. W. M.; Ho, K.-M. *J. Phys. Chem. A* **2000**, *104*, 6152. (c) Jarrold, M. F. *Annu. Rev. Phys. Chem.* **2000**, *51*, 179.