JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

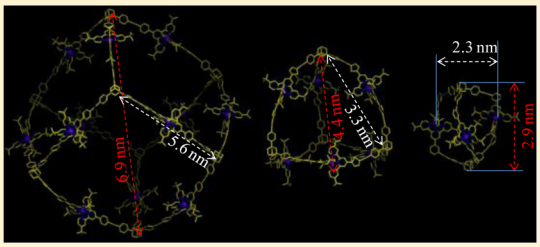
From Trigonal Bipyramidal to Platonic Solids: Self-Assembly and Self-Sorting Study of Terpyridine-Based 3D Architectures

Ming Wang,[†,∥] Chao Wang,[†,∥] Xin-Qi Hao,*[,‡] Xiaohong Li,[§] Tyler J Vaughn,[†] Yan-Yan Zhang,[#] Yihua Yu,[#] Zhong-Yu Li,[⊥] Mao-Ping Song,[‡] Hai-Bo Yang,[⊥] and Xiaopeng Li*[,†]

[†]Department of Chemistry and Biochemistry, Texas State University, San Marcos, Texas 78666, United States
[‡]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, China
[§]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China
[#]Shanghai Key Laboratory of Magnetic Resonance, Department of Physics and [⊥]Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

Supporting Information

ABSTRACT: Using a series of tritopic 2,2′:6′,2″-terpyridine (tpy) ligands constructed on adamantane, three discrete 3D metallo-supramolecular architectures were assembled, i.e., trigonal bipyramidal, tetrahedron, and cube. The self-assembly used tritopic ligands as corner directing units and metal ions as glue units at the edge. The angles of the linkers between adamantane and tpy head play a critical role in guiding the assembled structures, which have the general formula of $M_{3n}L_{2n}$, where M denotes metal ion and L denotes ligand. All complexes were fully characterized by ^{1}H, ^{13}C NMR, diffusion-ordered NMR spectroscopy, ESI-MS, and traveling-wave ion mobility-mass spectrometry. The binary mixtures of **LA** and **LC** or **LB** and **LC** underwent a self-sorting process that led to the self-assembly of discrete 3D structures. The self-sorting behavior is solely based on the angles precoded within the arm of tritopic ligands. Moreover, kinetic study of preassembled cube and tetrahedron demonstrated a slow ligand exchange process toward a statistical mixture of hetero tetrahedrons with **LA** and **LB**.



INTRODUCTION

Self-assembly of three-dimensional (3D) metallo-supramolecular cages have received considerable attention over the past two decades,[1−11] because of their applications in diverse fields such as host−guest chemistry,[12] molecular recognition,[13] reactivity modulation,[14] catalysis,[15] template synthesis,[16] and biology.[17] Such discrete 3D supramolecular architectures possess large void cavities and provide an ideal environment for the encapsulation of guest molecules. Therefore, control over the shape and size of 3D supramolecules has been one of the major driving forces for chemists working in the fields. Among these 3D architectures, there are two important species, platonic and archimedean polyhedra,[18] which could be constructed by carefully choosing the specific stoichiometry, the shape information instilled in the components and reaction conditions. In theory, if metal components act as vertices or corners of these polyhedra, organic ligands should become as edges or bridging units and *vice versa*.[1a,e] Actually, numerous polyhedral architectures were built with metals as vertices and ligands as edges, while polyhedral structures constructed by using organic ligands as directing units in the corners and metal components as edges were seldom reported.[1b−d] It is worth noting that the dodecahedron,[2a] adamantanoids,[2e] bipyramidal cage,[2c,19] and cavitand-based cage[20] reported by Stang, Fujita, and Dalcanale mainly used pyridine-based organic ligands as corner directing units and end-capped Pt(II) or Pd (II) components as edges.

Expanding self-assembly to 2,2′:6′,2″-terpyridine (tpy),[21] however, the construction of 3D architectures becomes even more challenging, mainly attributed to the following two reasons: (1) the fixed geometry of tpy-M(II)-tpy connectivity (i.e., 180°) and (2) the synthesis of appropriate organic ligands as directing units in the corners. Therefore, the self-assembly based on tpy was focused on supramolecular polymers,[22] macrocycles,[23] grid array,[24] and 2D architectures.[25] To date, very few 3D supramolecular cages and heteroleptic prisms were reported based on tpy-M(II)-tpy connectivity and the combination of terpyridine and bipyridine, respectively.[26] Considering that tpy-based supramolecular complexes have demonstrated remarkable utility in a myriad of applications, e.g., light harvesting devices, optical display devices, switches, molecular batteries,[27] the self-assembly of new 3D architectures using tpy building blocks may facilitate the design of novel synthetic materials with molecular level precision and high physical performance.

Due to the fixed ditopic geometry of tpy-M(II)-tpy connectivity, using multitopic tpy ligands as directing units becomes the only avenue toward 3D architectures. If tritopic

Received: May 29, 2014
Published: June 30, 2014

   dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

tpy ligands are designed with appropriate geometry, in theory, the possible structures of polyhedra have a general formula of $M_{3n}L_{2n}$ (M: metal ion; L: ligand), which are assembled by metal ions with these ligands at 2:3 ratio as proposed in Figure 1.

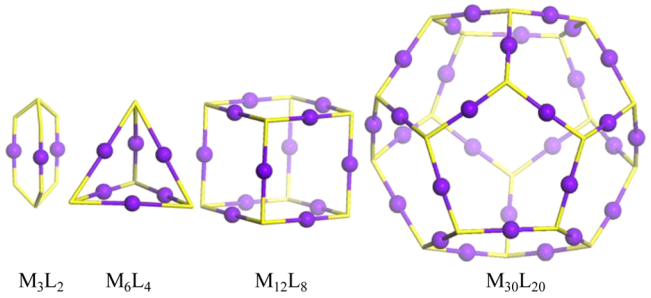


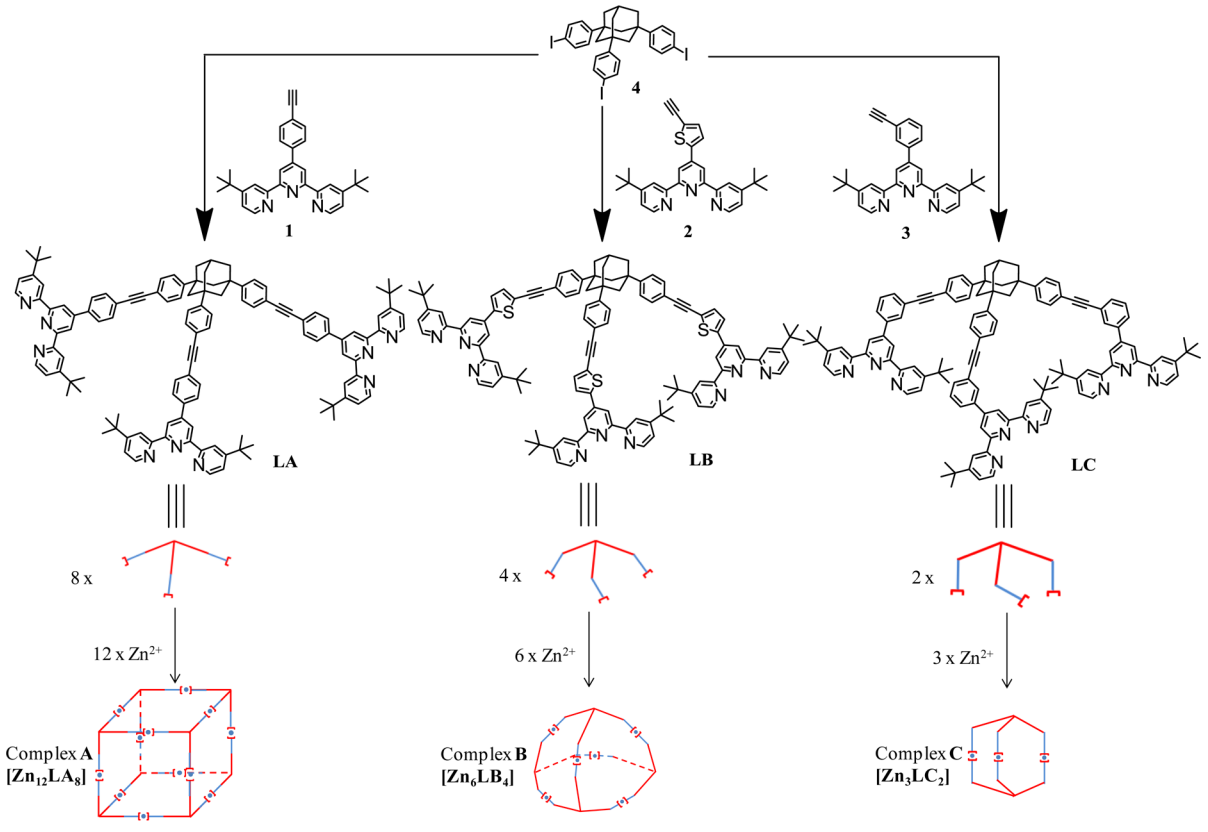
Figure 1. Self-assembly of of $\mathbf{M_{3n}L_{2n}}$ family with metals (**M**) as edges and tritopic ligands (**L**) as vertices, respectively.

Limited by geometrical constraints, *n* is limited to be 1, 2, 4 or 10, corresponding to bipyramidal-like dimer ($\mathbf{M_3L_2}$), tetrahedron ($\mathbf{M_6L_4}$), cube ($\mathbf{M_{12}L_8}$), and dodecahedron ($\mathbf{M_{30}L_{20}}$), respectively. The latter three belong to the platonic solids family. We initiated this study using a tritopic tpy ligand constructed on adamantane care as vertices and Zn(II) as gluing elements in the edges to assemble a supramolecular cube.[28] In contrast, we herein present the design and self-assembly of three discrete cages, i.e., bipyramidal-like dimer, tetrahedron, and cube by applying different linkers with appropriate angles between adamantane core and tpy units, such as *m*-phenyl, *p*-phenyl, and 2,5-thienyl (Scheme 1). Based on these discrete self-assembled 3D structures, we extended our study to investigate the self-sorting[29] behavior of this series of tritopic ligands. Finally, different cages were subjected for kinetic study to evaluate the stability of assembled cages.

RESULTS AND DISCUSSION

Synthesis and Self-Assembly of Complex A. We initially used Sonogashira coupling reaction to synthesize ligand **LA** with acetylene bond between adamantane and tpy (Scheme 1). Rather than the phenyl group in the previous study,[28] the extra acetylene was incorporated to increase the flexibility and reduce geometry constraints.[30] An elongated and flexible linker may become less capable of transmitting the directing effect of 109.5° provided by adamantane and thus, facilitates the self-assembly of small structures (i.e., dimer and tetrahedron). The bulky *t*-butyl moiety was introduced to increase the solubility of the assemblies and simplify the NMR spectra. Compounds **1** was directly accessible by the reaction between 4-((trimethylsilyl)ethynyl)benzaldehyde[31] and 1-(4-*tert*-butylpyridin-2-yl)ethanone[32] in a basic environment from a one-pot reaction (see Supporting Information). While forming the triketone intermediate species, desilylation also took place due to the existence of excess NaOH. The further ring-closure reaction with the addition of ammonium hydroxide gave **1** in a decent yield. Ligand **LA** was synthesized in a single step from **1** and 1,3,5,-tri(4-iodophenyl)-adamantane (**4**) in a reasonable yield by using Sonogashira coupling reaction and purified by column chromatography (Al_2O_3). Ligand **LA** was fully characterized by NMR (Figure 2) and ESI-MS. A stoichiometric ratio (2:3) of **LA** and $Zn(NO_3)_2{\cdot}6H_2O$ were mixed in $MeOH/CHCl_3$ at 50 °C for 8 h, followed by the addition of

Scheme 1. Synthetic Route of Ligands and Complexes $Zn_{3n}L_{2n}$



dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

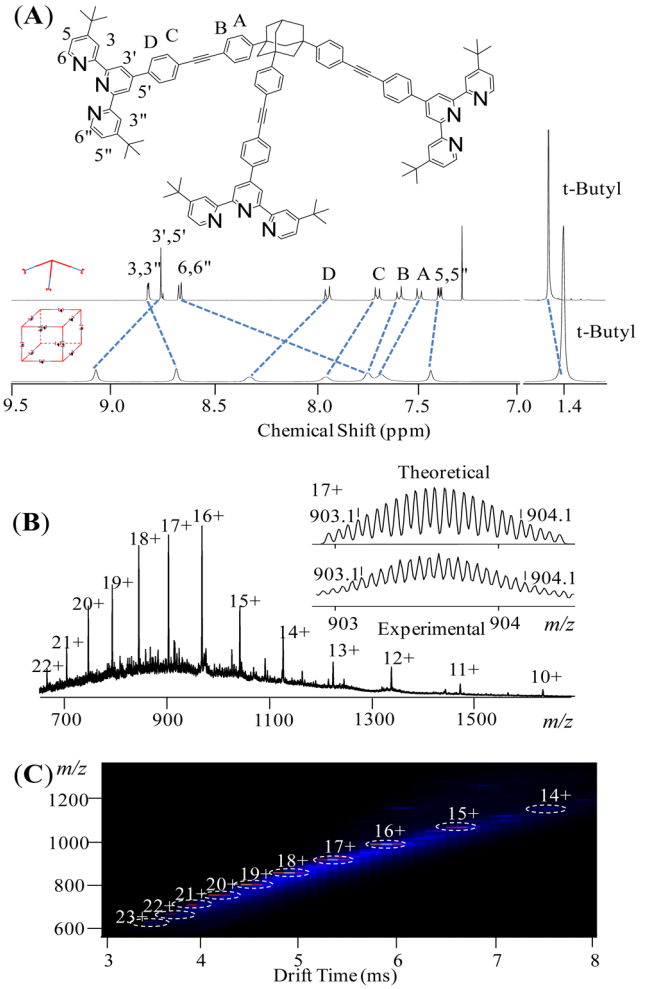


Figure 2. (A) ^{1}H NMR spectra (400 MHz) of ligand **LA** in $CDCl_3$ and complex **A** [$\mathbf{Zn_{12}LA_8}$] in CD_3CN. (B) ESI-MS and (C) 2D ESI-TWIM-MS plot (m/z vs drift time) of complex **A**. The charge states of intact assemblies are marked.

excess of NH_4PF_6 salt to give a white precipitate (complex **A**) after a thorough washing with water.

The ^{1}H NMR of complex **A** (Figure 2A) showed a simple pattern of peaks for a tpy-metal complex. In the aromatic region, there are eight sets of aromatic protons from tpy units and phenyl groups, as expected. The broad ^{1}H signals are typical for a large complex due to its slow tumbling motion on the NMR time scale.[3d] 3′,5′-tpy protons are significantly shifted to downfield, due to the lower electron density upon coordination with metal ions. Both the protons at 3,3″ and 6,6″ position of tpy shifted upfield (particularly for 6,6″ protons of tpy: $\Delta\delta$ = 0.95 ppm), which indicated the formation of complex with Zn(II), due to the electron shielding effect.[25a,d] The other hydrogen signals of aromatic protons were slightly shifted to downfield. The hydrogen signals of *t*-butyl group also showed a very sharp peak, suggesting a high degree of structural symmetry of the so-formed complex. The full assignments of ^{1}H NMR shown in Figure 2A were based on 2D-correlation spectroscopy (COSY) (see Figure S8). Heteronuclear single quantum correlation (HSQC) NMR spectrum also supported the generation of single structure with high symmetry and thus excluding other structural isomers (see Figure S10).

This complex was further characterized by ESI-MS and traveling-wave ion mobility-mass spectrometry (TWIM-MS) to determine the molecular composition and structural information.[23a,33] In ESI-MS (Figure 2B), one prominent set of peaks with charge states from 10+ to 22+ were observed (due to the loss of a different number of PF_6^-). And the isotope pattern of each peak closely matched the corresponding simulated isotope pattern of [$\mathbf{Zn_{12}LA_8}$] (Figure S1) for the desired cubic structure with molecular weight up to 17797.7 Da. It suggests that the arm of the ligand is flexible enough to accommodate the strain of the three-armed ligand under entropy-driven force by bending from 109.5° angle to 90°. In order to separate any superimposed fragments (i.e., tetrahedron) and detect the possible presence of overlapping isomers or conformers, TWIM-MS was introduced as the advanced level of MS analysis. As conventional ion mobility-mass spectrometry (IM-MS),[34] TWIM-MS is an effective approach to determine the analyte mass, charge, and shape by analyzing the drift time of an ion through the ion-mobility region (drift region).[23a,c,33] Typically, the compact ions drift faster than extended ions at the same charge state; while the high charge state ions drift faster than the low charge state ions at the same m/z. As shown in Figure 2C, each charge state of the formed cube [$\mathbf{Zn_{12}LA_8}$] was detected with narrow drift time distribution, indicating the absence of other isomers or structural conformers. The size information, i.e., experimental collision cross section (CCS),[35] was also calculated and correlated to the theoretical CCS obtained from molecular modeling (*vide infra*).

Synthesis and Self-Assembly of Complex B. Our initial study demonstrated that increasing the length of the linear linker between tpy and adamantane was not a feasible strategy to assemble smaller 3D structures, i.e., $\mathbf{M_3L_2}$ and $\mathbf{M_6L_4}$. Besides changing the length of linkers, we reasoned that incorporating suitable angular linkers would lead to the formation of possible smaller architectures. In light of this, we synthesized ligand **LB** (Figure 3) by introducing 2,5-thienyl with the bend angle 149°[36] to replace 1,4-phenyl (180°) linker used in **LA**. **2** was synthesized from 5-((trimethylsilyl)ethynyl)thiophene-2-carbaldehyde,[37] 1-(4-*tert*-butylpyridin-2-yl)ethanone, and NH_4OAc using a similar procedure as compound **1**. The use of NH_4OAc is to avoid the unexpected reduction of the acetylene bond into the alkene with the presence of ammonium hydroxide. The synthesis process of ligand **LB** and self-assembly of complex **B** followed the same procedure as ligand **LA** and complex **A**. The simple ^{1}H NMR pattern of complex **B** with one set of signals shows similar chemical shift to complex **A** (Figure 3A), indicating the formation of highly symmetric architecture. The 3,3″-tpy and 6,6″-tpy protons were shifted to upfield (particularly for 6,6″ protons of tpy: $\Delta\delta$ = 0.92 ppm) and all other peaks (tpy and phenyl) were slightly shifted to downfield. More structural evidences were provided by 2D-COSY and HSQC (see Figures S13 and S15).

Furthermore, ESI-MS (Figure 3B) and TWIM-MS (Figure 3C) spectra of complex **B** identified one discrete species. The corresponding isotope patterns observed were in well agreement with the calculated m/z ratios of tetrahedron (M_6L_4) with molecular weight at 8970.3 Da (Figure S2). The TWIM-MS spectrum (Figure 3C) clearly showed that no superimposed fragments, overlapping isomers, or conformers of the assembly existed in this complex. All these characterizations suggested that we obtained a smaller 3D tetrahedron architecture, viz., [$\mathbf{Zn_6LB_4}$], than cube by introducing the 2,5-thienyl groups between the adamantane core and tpy units to change the angles of the arms. It is worth noting that Newkome and co-workers recently reported a truncated tetrahedron assembled

dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

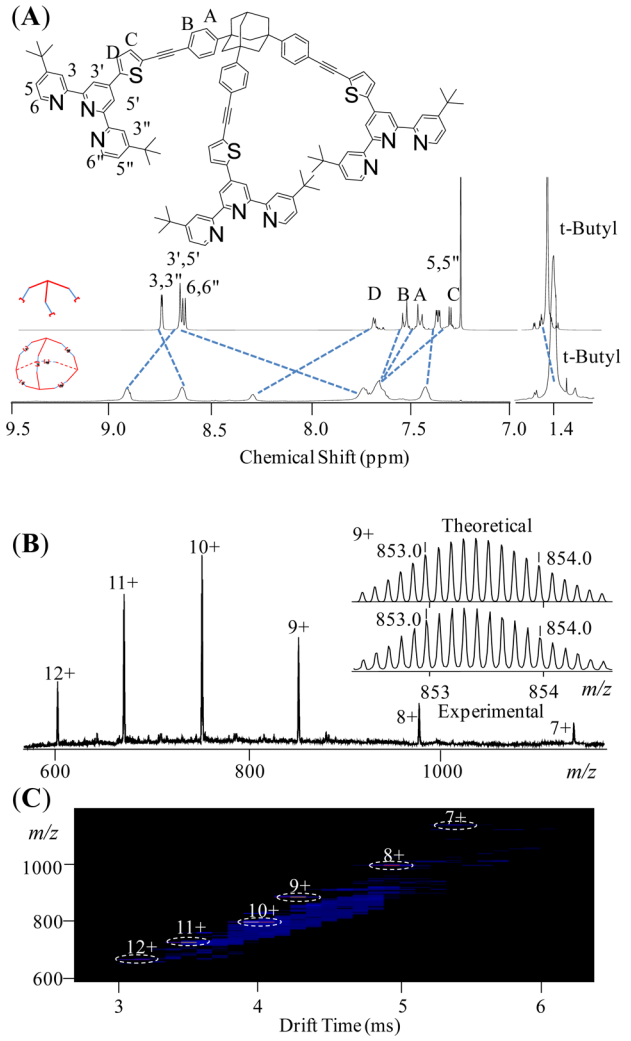


Figure 3. (A) ^{1}H NMR spectra (400 MHz) of ligand **LB** in $CDCl_3$ and complex **B** [$\mathbf{Zn_6LA_4}$] in CD_3CN. (B) ESI-MS and (C) 2D ESI-TWIM-MS plot (m/z vs drift time) of complex **B**. The charge states of intact assemblies are marked.

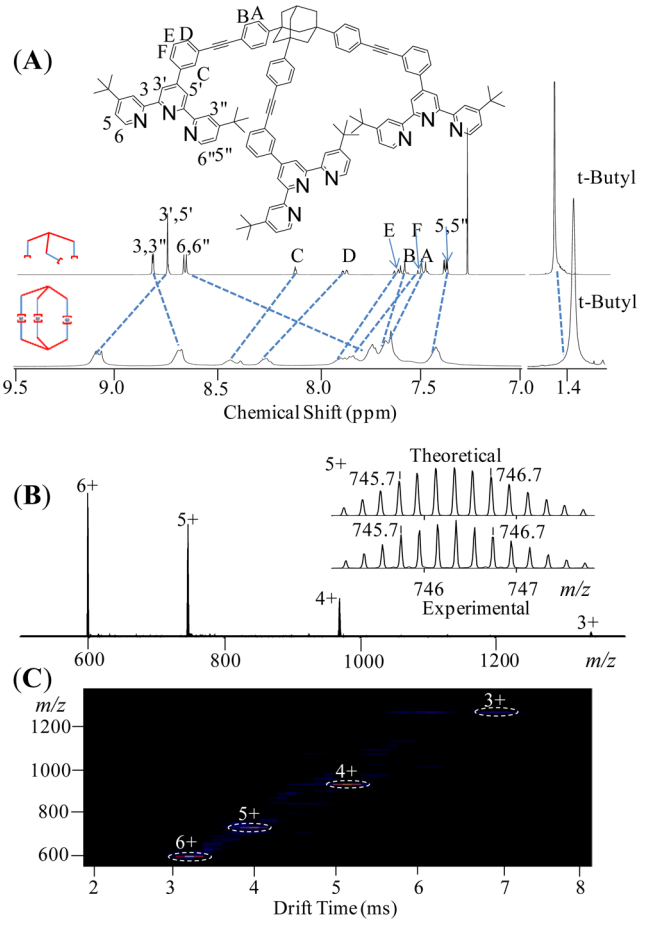


Figure 4. (A) ^{1}H NMR spectra (400 MHz) of ligand **LC** in $CDCl_3$ and complex **C** [$\mathbf{Zn_3LA_2}$] in CD_3CN. (B) ESI-MS and (C) 2D ESI-TWIM-MS plot complex **C** (m/z vs drift time). The charge states of intact assemblies are marked.

by tritopic terpyridine ligand and Ru(II) with smaller size using tris(4-bromophenyl)benzene as core structure and 1,3-phenyl as linker.[26f] Compared to the lower yield of Ru(II) truncated tetrahedron with column separation, our tetrahedron was directly obtained after self-assembly through precipitation with a decent yield (91%).

Synthesis and Self-Assembly of Complex C. Following this result, the introducing of 1,3-phenyl (120°) is considered as a feasible method to reach even smaller polyhedra dimer ($\mathbf{M_3L_2}$). 3-((trimethylsilyl)ethynyl)benzaldehyde[38] was used as starting material to synthesize **3**. As shown in Scheme 1, the synthesis route of ligand **LC** and complex **C** are the same as the synthesis of ligand **LA** and complex **A**. The ^{1}H NMR of complex **C** showed an expected upfield shift of 3,3″-tpy and 6,6″-tpy protons compared to ligand **LC**, according to the results of complex **A** and **B** (Figure 4A). The signals of the other peaks (tpy and phenyl) were shifted to downfield as expected.

ESI-MS (Figure 4B) and TWIM-MS (Figure 4C) spectra of complex **C** also showed trigonal bipyramidal as the sole product. The observed charge states of complex **C** (Z = 3+ to 6+) and the corresponding isotope patterns were shown in Figure S3. The calculated molecular weight was the same as the theoretical value of trigonal bipyramidal-like dimer at 4304.5 Da, from a series of prominent peaks by losing different numbers of counterions. From TWIM-MS spectra (Figure 3C), no superimposed fragments, overlapping isomers, or conformers of the assembly were found in complex **C**. All these results demonstrate that the complex **C** indeed possesses the trigonal bipyramidal-like architecture as expected.

Size Characterization by 2D DOSY NMR and CCS of TWIM-MS. Although these three polyhedra have been well documented by the NMR and MS results, all attempts to grow X-ray-quality single crystals have been proven to be unsuccessful to date. Alternatively, molecular simulation with Materials Studio showed distinct size differences of these complexes **A**, **B**, and **C**, which have diameters of 6.9, 4.4, and 2.9 nm, respectively (Figure 5). To validate these simulation results, diffusion-ordered NMR spectroscopy (DOSY) was used as an advanced technique to measure the trend of the size change and the results are shown in Figure 5. The observation of a single band at log D = −9.96, −9.66, and −9.48 for complexes **A**, **B**, and **C**, respectively, demonstrated the appreciable size decrease from complex **A** to complex **C**. These results confirmed the formation of three discrete 3D species after complexation of those different bridging ligands. In addition, this cube (complex **A**) with 5.6 nm edge length is

dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

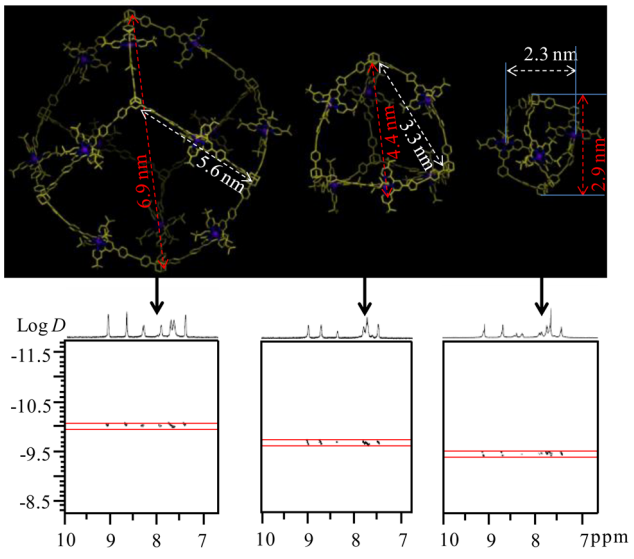


Figure 5. Energy-minimized structures of complexes **A** (left), **B** (middle), and **C** (right) from molecular modeling and 2D DOSY NMR spectra of complexes **A** (left), **B** (middle), and **C** (right) (500 MHz, CD_3CN, 300 K).

significantly larger than other metallo-supramolecular cubes reported in the literature.[39]

As another evidence, the TWIM-MS data were used to derive the collision cross sections (CCSs) of the ions being separated by ion mobility. The experimental CCS deduced from TWIM-IM was correlated to the theoretical CCS calculated from molecular modeling for cube and tetrahedron at various charge states (Table 1). Unfortunately, unlike linear drift tube IMS, TWIM-MS instruments require calibration using peptides or proteins ions of known CCSs to relate drift time.[33d,40] Further, this type of metallo-supramolecules may interact differently with the collision gas (N2) as compared to metal-free proteins. Despite the increasing use of commercial TWIM-MS instrumentation, there is not yet a suitable set of calibrants for metallo-supramolecular species to provide accurate experimental CCS from drift time data. Therefore, we used proteins as calibrants according to previous study by Wesdemiotis and Cronin.[23c,33b] Theoretical CCSs for 50 candidate structures of the $[Zn_{12}LA_8]$, $[Zn_6LB_4]$, and $[Zn_3LC_2]$ were calculated using the trajectory (TJ), which considers both long-range interactions and momentum transfer between the ions and the gas in the ion mobility region, and gives the most reliable CCS prediction.[35] The slight fluctuations of theoretical CCS indicated a highly rigid structure. It is worth mentioning that several leading groups in the metallo-supramolecular field, e.g., Lehn,[41] Stang,[42] and Fujita,[3c,30] have documented that the counterions are highly disoriented in crystals, and that their exact locations are unknown; for this reason, these groups have omitted counterions in the molecular modeling studies.[43] Furthermore, Bowers and co-workers showed that the experimental CCSs for the rectangle and triangle were nearly identical for the various charge states of these respective species. Adding or subtracting a counterion, had a negligible effect on the size of these complexes.[44] Given the giant size of our cube and tetrahedron and the number of counterions in the examined charge states (+14 to +23 for cube, +9 to +12 and tetrahedron), attempting to place the anions arbitrarily until structures are found that match the experimental CCS at each charge state is not tractable. Therefore, we omitted the counterions to simplify the structural modeling and theoretical CCS calculation.

Table 1. Experimental and Theoretical Collision Cross Sections (CCSs)

complex	drift times [ms]	CCS	CCS average	CCS (calcd avg) [Å^2]
A $[Zn_{12}LA_8]$	7.39(+14)	3126.2	3258.7 (149.8)[a]	3212.5 ± 43.3[b]
	6.50(+15)	3117.4		
	5.73 (+16)	3108.5		
	5.18 (+17)	3138.7		
	4.74(+18)	3184.4		
	4.41 (+19)	3251.5		
	4.19(+20)	3345.9		
	3.75 (+21)	3350.8		
	3.53(+22)	3425.8		
	3.42(+23)	3537.8		
B $[Zn_6LB_4]$	4.08 (+9)	1393.7	1510.9 (79.3)[a]	1599.8 ± 20.8[b]
	3.75 (+10)	1463.8		
	3.31 (+11)	1479.6		
	2.98(+12)	1502.2		
C $[Zn_3LC_2]$	6.73 (+3)	–	–	809.8 ± 12.4[b]
	4.96 (+4)	–		
	3.86 (+5)	–		
	3.09 (+6)	–		

[a]Average value of CCS. [b]TJ value obtained using MOBCAL.

Photophysical Properties. Normalized optical absorption and photoluminescence (PL) emission spectra of ligands and complexes (10^{-5} M) were shown in Figure S5. The maximum absorption peaks of these ligands and complexes are distinctly different (318 nm, 353 and 282 nm for ligand **LA**, **LB**, and **LC**; 342, 383, and 289 nm for complex **A**, **B**, and **C**, respectively.) The main absorption bands of ligands were associated with the $\pi-\pi^*$ transition through the conjugated backbone.[45] For complexes, the high-energy absorptions in the region between 250 and 400 nm are ligand-centered transitions ($\pi-\pi^*$).[46] The absorption spectra of ligand **LB** and complex **B** with thionyl units as linkers were obviously red-shifted than ligand **LA** and complex **A**, due to the donating-effect of the thienyl groups which lower the energy gap between HOMO and LUMO orbitals of the complex. In contrast, the spectra of **LC** and complex **C** were observed with the blue-shifted curve, due to the decrease of conjugation.[47] The PL emission spectra of these ligands and complexes also have similar differences (Figure S5b). It suggested that the introduction of different units with specific angles as the linker between adamantane core and tpy heads could get various 3D cage with different optical properties.

Self-Sorting Behavior. With all three discrete 3D structures, the next question raised by us is which structure

dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

forms in the case of a mixture of **LA**, **LB**, and/or **LC**. The ligands could exclusively self-sort into distinct complex **A**, **B**, and **C**, or else assemble into a statistical mixture. To answer this question, **LA** and **LC** were first mixed in equimolar ratio accompanied by stoichiometric amount of Zn(II) ions for the self-assembly in MeOH/$CHCl_3$ at 50 °C for 8 h, followed by the addition of excess of NH_4PF_6 salt to give a white precipitate. The ESI-MS and TWIM-MS results are depicted in Figure 6, showing distinguishable complex **A** and **C**. The

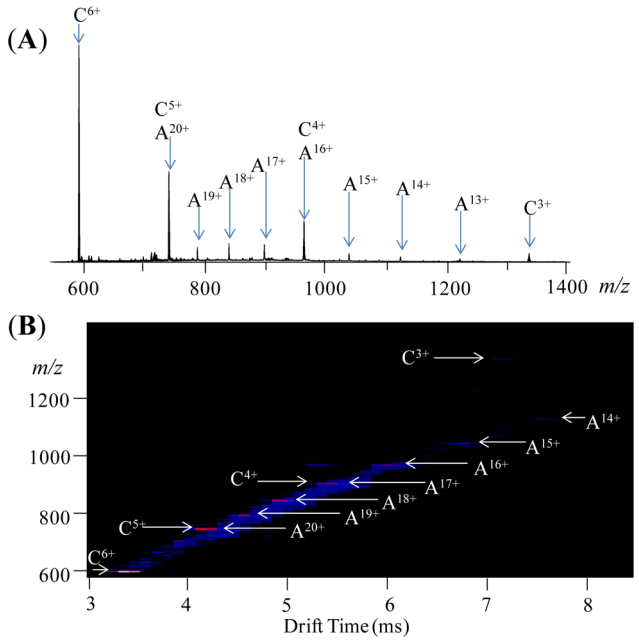


Figure 6. (A) ESI-MS and (B) 2D ESI-TWIM-MS plot of the complex assembled by **LA** and **LC** (m/z vs drift time). The charge states of intact assemblies are marked.

drift time of each ion at different charge states is consistent with the drift time obtained for individual complex in Figures 2 and 4, confirming that no statistical mixture of two ligands were assembled. Despite the possibility of forming myriad oligomeric structures and statistical mixture, discrete cube and trigonal bipyramidal were strongly preferred in the self-assembly, representative a self-sorting process.

Similarly, self-sorting behavior was also observed for a mixture of **LB** and **LC** at equimolar ratio. Both ESI-MS and TWIM-MS clearly showed distinguishable complexes **B** and **C** after self-assembly (Figure 7). The geometrical mismatch between **LA** and **LC** or **LB** and **LC** ligands disfavors hetero cage formation during the self-sorting process. Although numerous studies on self-sorting were reported, the self-sorting of 3D metallo-supramolecular structures was seldom addressed because spontaneous self-sorting of discrete structures out of a collection of multiple possibilities is always challenging. Among these 3D self-sorting, Stang[1c,48] and Dalcanale[20c] reported the size selective self-sorting of triangular prisms and cavitand-based coordination cages depending on the length of the pyridyl anchoring units. In contrast, the self-sorting behavior of our system is solely based on the angles of the tpy arms. Fujita and co-workers reported the self-assembly using a mixture of two angular ligands; however, a statistical mixture of cages was observed instead of discrete structures by self-sorting.[3d] Moreover, this is the first reported self-sorting study focusing on tpy-based 3D self-assembly in one pot.

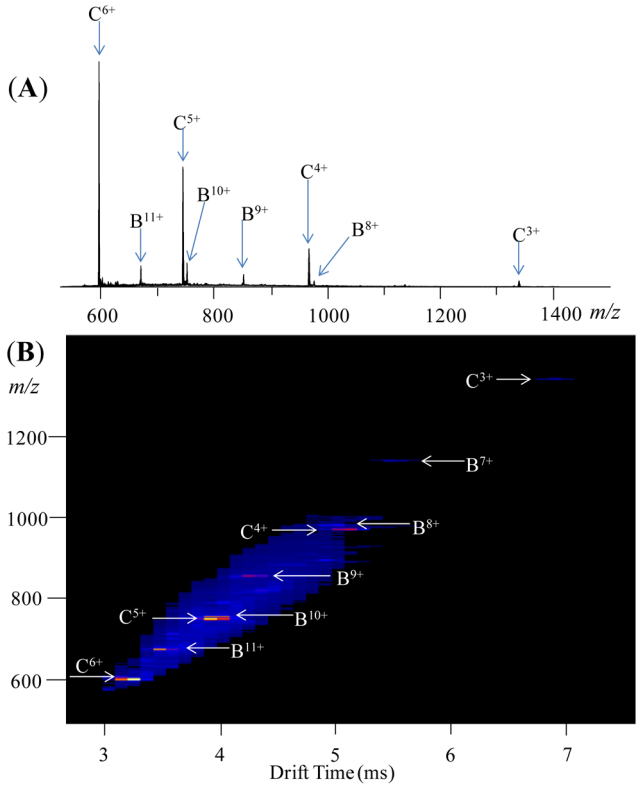


Figure 7. (A) ESI-MS and (B) 2D ESI-TWIM-MS plot of the complex assembled by **LB** and **LC** (m/z vs drift time). The charge states of intact assemblies are marked.

However, when **LA** and **LB** were mixed with equimolar ratio, a statistical mixture of tetrahedrons was observed in ESI-MS containing both ligands with a binomial distribution (Figure 8). It is interesting to note that the tetrahedron structure is more versatile and preferable than cube due to the composition of [$\mathbf{Zn_6LA_3LB}$]. Nevertheless, we were unable to give a plausible explanation for the formation of heterotetrahedron with **LA**

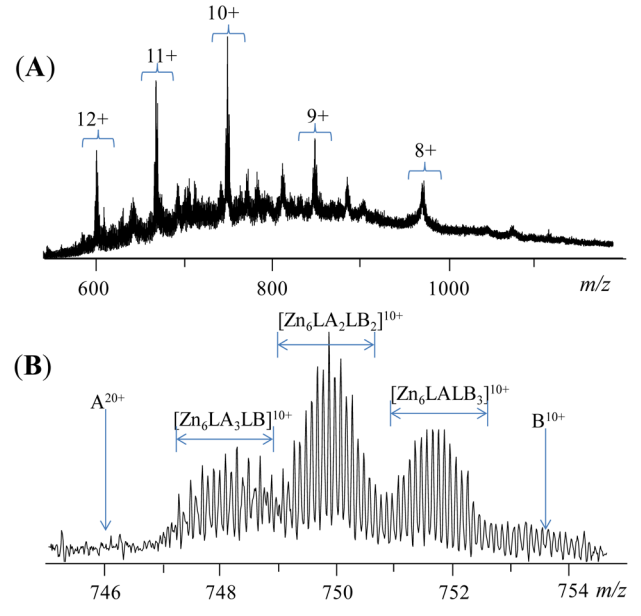


Figure 8. (A) ESI-MS spectrum of the complex assembled by **LA** and **LB**. (B) Enlarged spectrum of the region from m/z 746 to 754.

dx.doi.org/10.1021/ja505414x | J. Am. Chem. Soc. 2014, 136, 10499−10507

and **LB**, because of the angular difference of **LA** and **LB** is 31°, which is slightly large than that (i.e., 29°) of **LB** and **LC**.

Kinetic Study of Preassembled 3D Structures. Though the self-sorting behavior was not observed by mixing **LA** and **LB**, they were an ideal system to conduct kinetic study of preassembled complex **A** and **B**. The solution of preassembled complex **A** and **B** (CH_3CN, 1 mg/mL) were mixed at room temperature (1:1 by volume). The time dependent on ligands exchange and resulting structural change were monitored by the ESI-MS (Figure 9). After 5 h of mixing, the one-ligand-exchanged tetrahedron [$\mathbf{Zn_6LALB_3}$] was observed, indicating a slow ligand exchange process, which is consistent with the previous kinetic study of ligand exchange between two M12L24 cages by Fujita and co-workers.[49] After 7 days, all cube signals disappeared, however, heterocube with **LA** and **LB** was not detected, confirming the versatility of composition of tetrahedron. Overall, our kinetic study demonstrated the exceptional stability of preassembled 3D structures based on weak tpy-Zn(II)-tpy connectivity in the reassembly process.

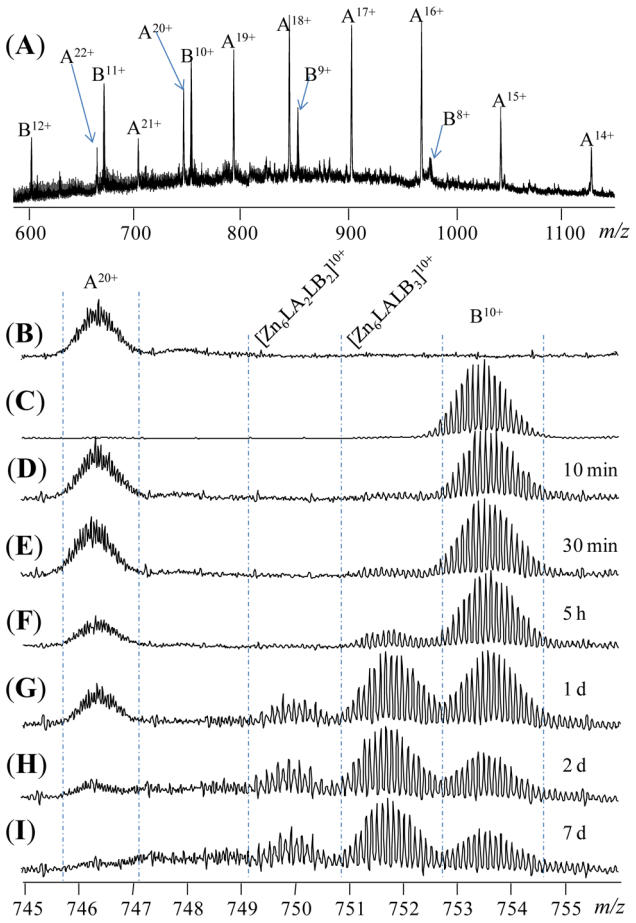


Figure 9. (A) The full ESI spectrum of the mixture of preassembled complex **A** and **B** at 0 min. Expanded regions show the 20+ signal for (B) pure **A** and 10+ signal for (C) pure **B** as control. Time-dependent spectra of mixing at preassembled complex **A** and **B** (D) 10 min, (E) 30 min, (F) 5 h, (G) 1 d, (H) 2 d, and (I) 7 d.

CONCLUSIONS

In conclusion, we designed and synthesized a series of tritopic ligands using adamantane and terpyridine with appropriate angular linkers, i.e., *p*-phenyl, 2,5-thienyl, and *m*-phenyl, to tune the self-assembly behavior. Discrete 3D metallo-supramolecules with a general formula of $M_{3n}L_{2n}$ including cube, tetrahedron, and trigonal bipyramidal-like dimer were obtained by employing these ligands as corner directing units and Zn^{2+} metal ions as edges, based on <tpy-Zn(II)-tpy> connectivity. NMR, ESI-MS, TWIM-MS, and DOSY unambiguously supported for the size, shape, and molecular composition. These results clearly demonstrate that the microscopic variations of directing geometry will result in the macroscopic differences for final 3D architectures. Furthermore, the binary mixtures of **LA** and **LC** or **LB** and **LC** underwent a self-sorting process that led to the self-assembly of discrete 3D structures. The self-sorting in our system is solely based on the angles precoded within the arm of tritopic ligands. Additionally, kinetic study of preassembled cube and tetrahedron demonstrated a slow ligand exchange process toward a statistical mixture of hetero tetrahedrons with **LA** and **LB**. Ongoing study of dodecahedron ($\mathbf{M_{30}L_{20}}$) is focused on the ligand design with shorter and more rigid linkers. More importantly, these cages may become an excellent system to study host–guest interaction due to their distinct cavity and face window sizes.

ASSOCIATED CONTENT

Supporting Information

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

AUTHOR INFORMATION

Corresponding Authors

X_L8@txstate.edu
xqhao@zzu.edu.cn

Author Contributions

‖These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Xiaopeng Li gratefully acknowledges the support from the Research Enhancement Program of Texas State University and the Welch Foundation (AI-0045). Xin-Qi Hao thanks the NSFC/China (No. 21102135) for financial support. Hai-Bo Yang thanks the NSFC/China (nos. 21132005 and 91027005) and the SMSTC (no. 13JC1402200) for financial support. Xiaohong Li thanks the NSFC/China (no. 21305098) and SRFDP (no. 20123201120014).

REFERENCES

(1) (a) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (b) Olenyuk, B.; Leininger, S.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (c) Northrop, B. H.; Zheng, Y.-R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554. (d) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (e) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (f) Harris, K.; Fujita, D.; Fujita, M. *Chem. Commun.* **2013**, *49*, 6703. (g) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (h) Pluth, M. D.; Raymond, K. N. *Chem. Soc. Rev.* **2007**, *36*, 161. (i) Müller, A.; Kögerler, P.; Dress, A. W. M. *Coord. Chem. Rev.* **2001**, *222*, 193. (j) Dalgarno, Scott J.; P, N. P.; Atwood, Jerry L. *Coord. Chem. Rev.* **2008**, *252*, 825. (k) Smulders, M. M.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728. (l) Lehn, J.-M. *Chem. Soc. Rev.* **2007**, *36*, 151. (m) Yoshizawa, M.; Klosterman, J. K.; Fujita,

M. *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 3418. (n) Saalfrank, R. W.; Maid, H.; Scheurer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8794.
(2) (a) Olenyuk, B.; Levin, M. D.; Whiteford, J. A.; Shield, J. E.; Stang, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434. (b) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796. (c) Radhakrishnan, U.; Schweiger, M.; Stang, P. J. *Org. Lett.* **2001**, *3*, 3141. (d) Kryschenko, Y. K.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 5193. (e) Leininger, S.; Fan, J.; Schmitz, M.; Stang, P. J. *Proc. Nat. Acad. Sci. U.S.A* **1999**, *97*, 1380. (f) Kuehl, C. J.; Kryschenko, Y. K.; Radhakrishnan, U.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Nat. Acad. Sci. U.S.A* **2002**, *99*, 4932. (g) Wang, M.; Zheng, Y.-R.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *50*, 6107. (h) Zheng, Y.-R.; Zhao, Z.; Wang, M.; Ghosh, K.; Pollock, J. B.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 16873. (i) Ghosh, K.; Hu, J.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 6695.
(3) (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469. (b) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52. (c) Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 5621. (d) Sun, Q.-F.; Iwasa, J.; Ogawa, D.; Ishido, Y.; Sato, S.; Ozeki, T.; Sei, Y.; Yamaguchi, K.; Fujita, M. *Science* **2010**, *328*, 1144. (e) Sun, Q.-F.; Murase, T.; Sato, S.; Fujita, M. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 10318.
(4) (a) Beissel, T.; Powers, R. E.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1084. (b) Caulder, D. L.; Brückner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923.
(5) (a) Meng, W.; Breiner, B.; Rissanen, K.; Thoburn, J. D.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 3479. (b) Bilbeisi, R. A.; Clegg, J. K.; Elgrishi, N.; Hatten, X. d.; Devillard, M.; Breiner, B.; Mal, P.; Nitschke, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 5110. (c) Riddell, I. A.; Hristova, Y. R.; Clegg, J. K.; Wood, C. S.; Breiner, B.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 2723. (d) Zarra, S.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 4837.
(6) (a) Fowler, D. A.; Mossine, A. V.; Beavers, C. M.; Teat, S. J.; Dalgarno, S. J.; Atwood, J. L. *J. Am. Chem. Soc.* **2011**, *133*, 11069. (b) Fowler, D. A.; Rathnayake, A. S.; Kennedy, S.; Kumari, H.; Beavers, C. M.; Teat, S. J.; Atwood, J. L. *J. Am. Chem. Soc.* **2013**, *135*, 12184.
(7) (a) Hiraoka, S.; Harano, K.; Shiro, M.; Ozawa, Y.; Yasuda, N.; Toriumi, K.; Shionoya, M. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 6488. (b) Hiraoka, S.; Harano, K.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2008**, *130*, 14368. (c) Hiraoka, S.; Yamauchi, Y.; Arakane, R.; Shionoya, M. *J. Am. Chem. Soc.* **2009**, *131*, 11646.
(8) (a) Engelhard, D. M.; Freye, S.; Grohe, K.; John, M.; Clever, G. H. *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 4747. (b) Frank, M.; Hey, J.; Balcioglu, I.; Chen, Y.-S.; Stalke, D.; Suenobu, T.; Fukuzumi, S.; Frauendorf, H.; Clever, G. H. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 10102.
(9) (a) Chepelin, O.; Ujma, J.; Barran, P. E.; Lusby, P. J. *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 4194. (b) Lusby, P. J.; Müller, P.; Pike, S. J.; Slawin, A. M. Z. *J. Am. Chem. Soc.* **2009**, *131*, 16398.
(10) (a) Li, J.-R.; Zhou, H.-C. *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 8465. (b) Li, J.-R.; Timmons, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 6368. (c) Li, J.-R.; Zhou, H.-C. *Nat. Chem.* **2010**, *2*, 893. (d) Li, J.-R.; Yakovenko, A. A.; Lu, W.; Timmons, D. J.; Zhuang, W.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2010**, *132*, 17599. (e) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nat. Commun.* **2013**, *4*, 1538.
(11) (a) Mahata, K.; Frischmann, P. D.; Würthner, F. *J. Am. Chem. Soc.* **2013**, *135*, 15656. (b) Stephenson, A.; Argent, S. P.; Riis-Johannessen, T.; Tidmarsh, I. S.; Ward, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 858. (c) Granzhan, A.; Schouwey, C.; Riis-Johannessen, T.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2011**, *133*, 7106. (d) Mirtschin, S.; Slabon-Turski, A.; Scopelliti, R.; Velders, A. H.; Severin, K. *J. Am. Chem. Soc.* **2010**, *132*, 14004. (e) Yamanaka, M.; Kawaharada, M.; Nito, Y.; Takaya, H.; Kobayashi, K. *J. Am. Chem. Soc.* **2011**, *133*, 16650.
(12) (a) Smulders, M. M. J.; Zarra, S.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 7039. (b) Mugridge, J. S.; Zahl, A.; Eldik, R. v.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2013**, *135*, 4299. (c) Han, M.; Michel, R.; He, B.; Chen, Y.-S.; Stalke, D.; John, M.; Clever, G. H. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 1319. (d) Sánchez-Molina, I.; Grimm, B.; Calderon, R. M. K.; Claessens, C. G.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2013**, *135*, 10503. (e) Zheng, Y.-R.; Lan, W.-J.; Wang, M.; Cook, T. R.; Stang, P. J. *J. Am. Chem. Soc.* **2011**, *133*, 17045. (f) Zheng, Y.-R.; Zhao, Z.; Kim, H.; Wang, M.; Ghosh, K.; Pollock, J. B.; Chi, K.-W.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *49*, 10238.
(13) (a) Sato, S.; Iida, J.; Suzuki, K.; Kawano, M.; Ozeki, T.; Fujita, M. *Science* **2006**, *313*, 1273. (b) Freye, S.; Michel, R.; Stalke, D.; Pawliczek, M.; Frauendorf, H.; Clever, G. H. *J. Am. Chem. Soc.* **2013**, *135*, 8476. (c) Yoshizawa, M.; Tamura, M.; Fujita, M. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 3874. (d) Wang, M.; Vajpayee, V.; Shanmugaraju, S.; Zheng, Y.-R.; Zhao, Z.; Kim, H.; Mukherjee, P. S.; Chi, K.-W.; Stang, P. J. *Inorg. Chem.* **2011**, *50*, 1506.
(14) (a) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* **2009**, *324*, 1697. (b) Nishioka, Y.; Yamaguchi, T.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2008**, *130*, 8160. (c) Murase, T.; Sato, S.; Fujita, M. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 1083. (d) Smulders, M. M. J.; Nitschke, J. R. *Chem. Sci.* **2012**, *3*, 785.
(15) (a) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251. (b) Murase, T.; Horiuchi, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2866. (c) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Science* **2007**, *316*, 85. (d) Bolliger, J. L.; Belenguer, A. M.; Nitschke, J. R. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 7958. (e) Zhao, C.; Sun, Q.-F.; Hart-Cooper, W. M.; DiPasquale, A. G.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2013**, *135*, 18802.
(16) (a) Suzuki, K.; Sato, S.; Fujita, M. *Nat. Chem.* **2010**, *2*, 25. (b) Takao, K.; Suzuki, K.; Ichijo, T.; Sato, S.; Asakura, H.; Teramura, K.; Kato, K.; Ohba, T.; Morita, T.; Fujita, M. *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 5893. (c) Ichijo, T.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2013**, *135*, 6786−6789.
(17) (a) Tashiro, S.; Tominaga, M.; Kawano, M.; Therrien, B.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 4546. (b) Fujita, D.; Suzuki, K.; Sato, S.; Yagi-Utsumi, M.; Yamaguchi, Y.; Mizuno, N.; Kumasaka, T.; Takata, M.; Noda, M.; Uchiyama, S.; Kato, K.; Fujita, M. *Nat. Commun.* **2012**, *3*, 1093. (c) Vajpayee, V.; Lee, S. m.; Park, J. W.; Dubey, A.; Kim, H.; Cook, T. R.; Stang, P. J.; Chi, K.-W. *Organometallics* **2013**, *32*, 1563.
(18) Torquato, S.; Jiao, Y. *Nature* **2009**, *460*, 876.
(19) (a) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649. (b) Mukherjee, P. S.; Das, N.; Stang, P. J. *J. Org. Chem.* **2004**, *69*, 3526.
(20) (a) Jacopozzi, P.; Dalcanale, E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 613. (b) Fochi, F.; Jacopozzi, P.; Wegelius, E.; Rissanen, K.; Cozzini, P.; Marastoni, E.; Fisicaro, E.; Manini, P.; Fokkens, R.; Dalcanale, E. *J. Am. Chem. Soc.* **2001**, *123*, 7539. (c) Pinalli, R.; Cristini, V.; Sottili, V.; Geremia, S.; Campagnolo, M.; Caneschi, A.; Dalcanale, E. *J. Am. Chem. Soc.* **2004**, *126*, 6516. (d) Zuccaccia, D.; Pirondini, L.; Pinalli, R.; Dalcanale, E.; Macchioni, A. *J. Am. Chem. Soc.* **2005**, *127*, 7025.
(21) (a) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2892. (b) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373. (c) Wild, A.; Winter, A.; Schlütter, F.; Schubert, U. S. *Chem. Soc. Rev.* **2011**, *40*, 1459. (d) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (e) Constable, E. C. *Coord. Chem. Rev.* **2008**, *252*, 842. (f) De, S.; Mahata, K.; Schmittel, M. *Chem. Soc. Rev.* **2010**, *39*, 1555. (g) Eryazici, I.; Moorefield, C. N.; Newkome, G. R. *Chem. Rev.* **2008**, *108*, 1834.
(22) (a) Shunmugam, R.; Tew, G. N. *J. Am. Chem. Soc.* **2005**, *127*, 13567. (b) Zhang, K.; Zha, Y.; Peng, B.; Chen, Y.; Tew, G. N. *J. Am. Chem. Soc.* **2013**, *135*, 15994. (c) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913. (d) Bode, S.; Zedler, L.; Schacher, F. H.; Dietzek, B.; Schmitt, M.;

Popp, J.; Hager, M. D.; Schubert, U. S. *Adv. Mater.* **2013**, *25*, 1634. (e) Fermi, A.; Bergamini, G.; Roy, M.; Gingras, M.; Ceroni, P. *J. Am. Chem. Soc.* **2014**, *136*, 6395.
(23) (a) Chan, Y.-T.; Li, X.; Soler, M.; Wang, J.-L.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2009**, *131*, 16395. (b) Perera, S.; Li, X.; Soler, M.; Wesdemiotis, C.; Moorefield, C. N.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 6539. (c) 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. (d) Chan, Y.-T.; Li, X.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem.—Eur. J.* **2011**, *17*, 7750. (e) Mahata, K.; Saha, M. L.; Schmittel, M. *J. Am. Chem. Soc.* **2010**, *132*, 15933. (f) Mahata, K.; Schmittel, M. *J. Am. Chem. Soc.* **2009**, *131*, 16544.
(24) (a) Salditt, T.; An, Q.; Plech, A.; Eschbaumer, C.; Schubert, U. S. *Chem. Commun.* **1998**, 2731. (b) Bassani, D. M.; Lehn, J.-M.; Fromm, K.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2364. (c) Barboiu, M.; Vaughan, G.; Graff, R.; Lehn, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 10257.
(25) (a) Lu, X.; Li, X.; Cao, Y.; Schultz, A.; Wang, J.-L.; Moorefield, C. N.; Wesdemiotis, C.; Cheng, S. Z. D.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 7728. (b) Schultz, A.; Li, X.; Barkakaty, B.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2012**, *134*, 7672. (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) 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. (e) Zheng, Z.; Opilik, L.; Schiffmann, F.; Liu, W.; Bergamini, G.; Ceroni, P.; Lee, L.-T.; Schütz, A.; Sakamoto, J.; Zenobi, R.; VandeVondele, J.; Schlüter, A. D. *J. Am. Chem. Soc.* **2014**, *136*, 6103. (f) Wang, M.; Wang, C.; Hao, X.-Q.; Liu, J.; Li, X.; Xu, C.; Lopez, A.; Sun, L.; Song, M.-P.; Yang, H.-B.; Li, X. *J. Am. Chem. Soc.* **2014**, *136*, 6664.
(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) Schmittel, M.; He, B.; Mal, P. *Org. Lett.* **2008**, *10*, 2513. (c) Schmittel, M.; He, B. *Chem. Commun.* **2008**, 4723. (d) Samanta, S. K.; Schmittel, M. *Org. Biomol. Chem.* **2013**, *11*, 3108. (e) Cardona-Serra, S.; Coronado, E.; Gaviña, P.; Poncea, J.; Tatay, S. *Chem. Commun.* **2011**, *47*, 8235. (f) Xie, T.-Z.; Liao, S.-Y.; Guo, K.; Lu, X.; Dong, X.; Huang, M.; Moorefield, C. N.; Cheng, S. Z. D.; Liu, X.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2014**, *136*, 8165.
(27) (a) Brown, D. G.; Sanguantrakun, N.; Schulze, B.; Schubert, U. S.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2012**, *134*, 12354. (b) Chou, C.-C.; Wu, K.-L.; Chi, Y.; Hu, W.-P.; Yu, S. J.; Lee, G.-H.; Lin, C.-L.; Chou, P.-T. *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 2054. (c) Winter, A.; Hager, M. D.; Newkome, G. R.; Schubert, U. S. *Adv. Mater.* **2011**, *23*, 5728. (d) Winter, A.; Hoeppener, S.; Newkome, G. R.; Schubert, U. S. *Adv. Mater.* **2011**, *23*, 3484.
(28) Wang, C.; Hao, X.-Q.; Wang, M.; Guo, C.; Xu, B.; Tan, E. N.; Zhang, Y.-Y.; Yu, Y.; Li, Z.-Y.; Yang, H.-B.; Song, M.-P.; Li, X. *Chem. Sci.* **2014**, *5*, 1221.
(29) (a) Lehn, J.-M. *Science* **2002**, *295*, 2400. (b) Wu, A.; Isaacs, L. *J. Am. Chem. Soc.* **2003**, *125*, 4831.
(30) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535.
(31) (a) Chen, Y.; Wu, Y.; Henklein, P.; Li, X.; Hofmann, K. P.; Nakanishi, K.; Ernst, O. P. *Chem.—Eur. J.* **2010**, *16*, 7389. (b) Wang, X.; Ervithayasuporn, V.; Zhang, Y.; Kawakami, Y. *Chem. Commun.* **2011**, *47*, 1282.
(32) Perera, S.; Li, X.; Guo, M.; Wesdemiotis, C.; Moorefield, C. N.; Newkome, G. R. *Chem. Commun.* **2011**, *47*, 4658.
(33) (a) Ujma, J.; Cecco, M. D.; Chepelin, O.; Levene, H.; Moffat, C.; Pike, S. J.; Lusby, P. J.; Barran, P. E. *Chem. Commun.* **2012**, *48*, 4423. (b) 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. Engl.* **2011**, *123*, 9033. (c) Scarff, C. A.; Snelling, J. R.; Knust, M. M.; Wilkins, C. L.; Scrivens, J. H. *J. Am. Chem. Soc.* **2012**, *134*, 9193. (d) Ruotolo, B. T.; Benesch, J. L. P.; Sandercock, A. M.; Hyung, S.-J.; Robinson, C. V. *Nat. Protoc.* **2008**, *3*, 1139.
(34) (a) Brocker, 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.; Helden, G. v.; Koppen, P. A. M. v. *Science* **1993**, *260*, 1446. (c) Trimpin, S.; Plasencia, M.; Isailovic, D.; Clemmer, D. E. *Anal. Chem.* **2007**, *79*, 7965. (d) 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.
(35) (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.
(36) Bunzen, J.; Iwasa, J.; Bonakdarzadeh, P.; Numata, E.; Rissanen, K.; Sato, S.; Fujita, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3161.
(37) Fillaut, J.-L.; Perruchon, J.; Blanchard, P.; Roncali, J.; Golhen, S.; Allain, M.; Migalsaka-Zalas, A.; Kityk, I. V.; Sahraoui, B. *Organometallics* **2005**, *24*, 687.
(38) (a) Tanasova, M.; Borhan, B. *Eur. J. Org. Chem.* **2012**, 3261. (b) Frixa, C.; Mahon, M. F.; Thompson, A. S.; Threadgill, M. D. *Org. Biomol. Chem.* **2003**, *1*, 306.
(39) (a) Roche, S.; Haslam, C.; Adams, H.; Heath, S. L.; Thomas, J. A. *Chem. Commun.* **1998**, 1681. (b) Klausmeyer, K. K.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1694. (c) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 2705. (d) Tidmarsh, I. S.; Faust, T. B.; Adams, H.; Harding, L. P.; Russo, L.; Clegg, W.; Ward, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 15167.
(40) Thalassinos, K.; Grabenauer, M.; Slade, S. E.; Hilton, G. R.; Bowers, M. T.; Scrivens, J. H. *Anal. Chem.* **2009**, *81*, 248.
(41) (a) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **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.
(42) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3467.
(43) (a) Lee, J.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 12028. (b) Wang, M.; Zheng, Y. R.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 6282. (c) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239.
(44) Anderson, S. E.; Bleiholder, C.; Brocker, E. R.; Stang, P. J.; Bowers, M. T. *Int. J. Mass Spectrom.* **2012**, *330*−*332*, 78.
(45) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1366.
(46) Beley, M.; Delabouglise, D.; Houppy, G.; Husson, J.; Petit, J.-P. *Inorg. Chim. Acta* **2005**, *358*, 3075.
(47) (a) Higuchi, J.; Hayashi, K.; Yagi, M.; Kondo, H. *J. Phys. Chem. A* **2002**, *106*, 8609. (b) Higuchi, J.; Hayashi, K.; Seki, K.; Yagi, M.; Ishizu, K.; Kohno, M.; Ibuki, E.; Tajima, K. *J. Phys. Chem. A* **2001**, *105*, 6084.
(48) (a) Zheng, Y.-R.; Yang, H.-B.; Northrop, B. H.; Ghosh, K.; Stang, P. J. *Inorg. Chem.* **2008**, *47*, 4706. (b) Zheng, Y.-R.; Yang, H.-B.; Ghosh, K.; Zhao, L.; Stang, P. J. *Chem.—Eur. J.* **2009**, *15*, 7203.
(49) Sato, S.; Ishido, Y.; Fujita, M. *J. Am. Chem. Soc.* **2009**, *131*, 6064.