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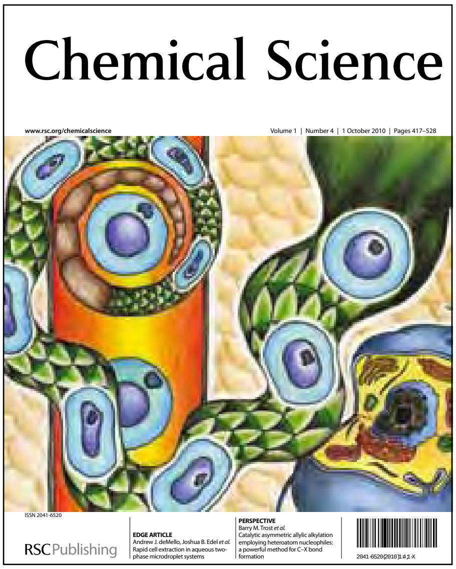
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Self-Assembly of Giant Supramolecular Cubes with Terpyridine Ligands as Vertices and Metals on Edges

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Self-assembly of three-dimensional (3-D) architecture using terpyridine (tpy)-based building blocks is challenging and seldom addressed due the fixed geometry (around 180°) of tpy-M(II)-tpy (M = Ru, Fe, Zn, and Cd) connectivity. Here we describe the self-assembly of 3-D giant metallo-supramolecular cubes using three-armed terpyridine ligands constructed on adamantane with molecular weight up to 18k and edge length at ~4.9 nm, which is significantly larger than the sizes of previous metallo-supramolecular cubes. Instead of using metal center as vertices in the commonly used synthetic strategy of 3-D molecular coordination ensembles, these cages [$\mathbf{M_{12}L_8}$] bear 8 ligands as vertices with 12 metal ions on the edges. With a suitable edge length, the giant cubes appear to be the sole product after self-assembly from a variety of possible architectures. The 3-D metallo-supramolecules were characterized and supported by NMR, DOSY, ESI-MS, traveling wave ion mobility-mass spectrometry (TWIM-MS) and AFM.

Introduction

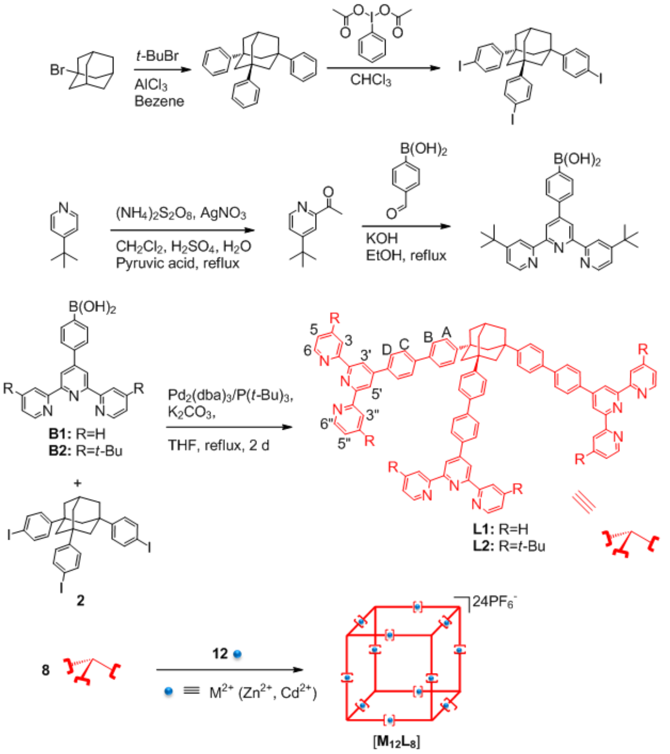
The spontaneous self-assembly of one or more subunits is common in nature to create different biological systems with well-defined architectures.[1] Due to the highly directional and predictable feature of the metal coordination, metal-mediated self-assembly acts as a powerful tool to mimic nature's activities.[2] This has been used as a chemical approach for construction of a series of 3-D structures with precise geometries and sizes.[3,4] Among these 3-D structures, in particular for Pt(II) and Pd(II)-mediated self-assembly with pyridyl ligands, the coordination geometry of the metal ions and angle of ligands play vital roles in guiding the topologies of the final architectures. In most circumstances, end-capped metal components or naked metal ions were used as corner units and organic ligands were incorporated into the edges. Like enzymes, these 3-D structures act as catalysts or molecular flasks for reactions that fit the shape of the confined space.[5] The microenvironment inside 3-D structures can also enhance intermolecular interactions and stabilize reactive intermediates.[6,7] While the initial focus was on the encapsulation of small molecules or ions, recent research efforts have shifted to designing larger 3-D architectures that are capable of encapsulating inorganic catalysts, larger substrates, and even small proteins.[8]

2,2':6',2"-terpyridine (tpy)-based subunits attract considerable attention in the coordination-driven approach for supramolecular self-assemblies, due to their inherent ability to bind different transition metal ions strongly and the relative ease for constructing multi-nuclear complexes.[9] However, the connectivity of tpy-M(II)-tpy (M = Ru, Fe, Zn, and Cd) is generally fixed at 180° and thus, limits the use of metal ions as cornered directing units. Therefore, many previous studies of tpy-M(II)-tpy only concentrated on linear and 2-D structures compared to the numerous reports of 3-D structures based on pyridine.[9,10] Up to date, a few 3-D supramolecular cages and prisms were reported using tpy-based building blocks to the best of our knowledge.[11] We herein, for the first time, utilize tpy-based organic ligand built on adamantane as directing unit in the vertices to construct giant 3-D supramolecular cubes possessing highly symmetric structure with metal ions on edges, which could be potentially useful in cavity-templated synthesis[6] and guest encapsulation[7].

A strategic design with coordination-driven self-assembly of the supramolecular cube [$\mathbf{M_{12}L_8}$] (Figure 1) is outlined in Scheme 1. The construction of the cubic cages only required 12 metal ions and 8 three-armed building blocks. The three-armed ligand was designed by incorporating three tpy groups into rigid adamantane core, which provides 109°28' geometry based on sp^3 hybridization at its points of bisection. When the three-armed ligands and metal ions are mixed together with the correct ratio (2:3) in a non-coordinating solvent, these components will go through exchange processes of possible intermediate states and finally reach the most thermodynamically stable states. Based on the geometry of Platonic solids,[12] we reasoned that both cube and dodecahedron could be formed using this ligand with high possibility. Entropically, structures of smaller size are more favourable (*i.e.*, cube). However, a smaller self-assembly like cube structure would require the arms of the ligand to bend to at least a mutual 90˚ angle as they are bonded to metal ions. This seems unlikely to happen since the twisting of those arms from 109˚28' angle to 90˚ angle will produce a strained substructure. Nevertheless, it has been demonstrated theoretically and experimentally that it is possible for rigid aromatic rings to bend a certain small angle.[13] Unpredicted structures often appear because organic ligands are much more flexible than expected and metal centers can also permit considerable deviation in their coordination angles.[14] Hence, instead of forming a large dodecahedron with 108˚ angle, we predicted that the cubic geometry as the smaller ensemble can be formed because the linker between adamantane and terpyridine may provide enough flexibility to accommodate the strain of the three-armed ligand. We hypothesized that these symmetric cubic cages would be more thermodynamically stable than other assembles (e.*g.*, dodecahedron) if appropriate length of linker between adamantane and terpyridine was applied.

Results and discussion

Synthetic procedures



Scheme 1. Synthetic route to the ligands and [$\mathbf{M_{12}L_8}$].

Under this hypothesis, **L1** was chosen in our initial efforts as the candidate ligand, which has the same structure with **L2** but without bulky *t*-butyl groups. 1,3,5-triphenyl-adamantane[15], 1,3,5-tri(4-iodophenyl)-adamantane[16] **2** and 4'-(4-Boronatophenyl)-[2,2':6',2"]terpyridine[10b] **B1** were prepared according to literature procedure. Ligand **L1** was synthesized from **B1** and **2** by Suzuki coupling reaction using $Pd_2(dba)_3$ and P(*t*-Bu)$_3$ as catalyst. Although the self-assembly with $\mathbf{Zn_{12}L1_8}$ composition was observed by ESI-MS (see Figure 1), the low solubility of both ligand and complex obstructed further characterization by common techniques such as NMR to unambiguously prove the cubic structure. Therefore, the three-armed ligand **L2** was redesigned to bring bulky *t*-butyl moieties to increase the solubility of the assemblies and simplify the NMR spectra. Note that the bumpy baseline of the mass spectrum in Figure 1 is mainly because of the low intensity of signal due to the low solubility of $\mathbf{M_{12}L1_8}$ and the encapsulation of solvent or salt molecules inside the cube.

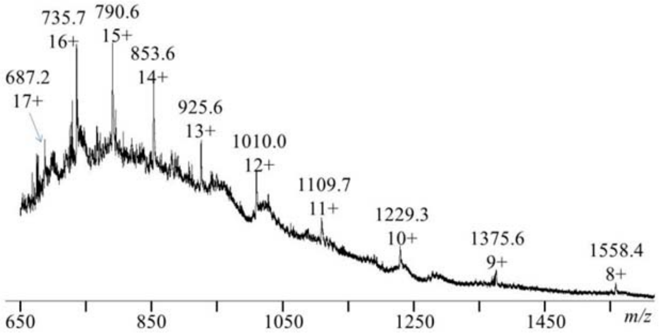


Figure 1. ESI mass spectrum for [$\mathbf{Zn_{12}L1_8}$].The different charge states ions were derived from losing different numbers of counter-ions.

Boronic acid **B2** was synthesized from 4-formyl-phenylboronic acid and 2-acetyl-4-*t*-butylpyridine. Ligand **L2** was synthesized similarly as **L1** by Suzuki coupling of **B2** and **2**. Due to the existence of bulky *t*-butyl groups, not only the solubility of **L2** had increased significantly, but also the ^{1}H NMR was easily discernible compared to the ligand without *t*-butyl groups (see supporting information). Ligand **L2** was fully characterized by NMR and ESI-MS. In the aromatic region of ^{1}H NMR (Figure 2), there was only one set of protons for tpy and a sharp singlet at 1.48 ppm that was assigned to the bulky *t*-butyl groups.

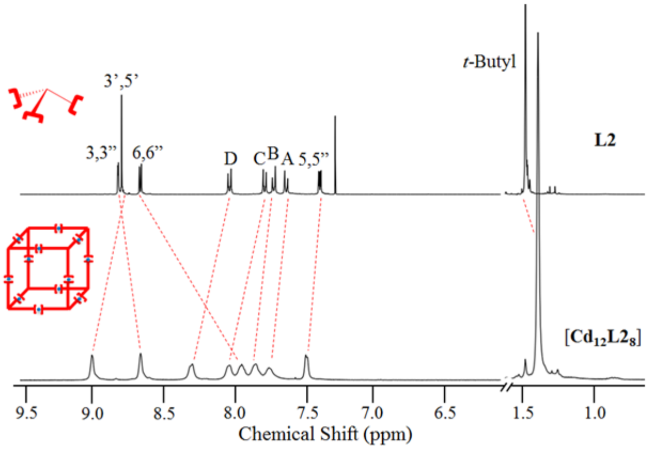


Figure 2. ^{1}H NMR spectra (400 MHz) of ligand **L2** in $CDCl_3$ and [$\mathbf{Cd_{12}L2_8}$] in CD_3CN.

In one simple step, 8 three-armed ligand 'corners' and 12 octahedral metal edges come together to simultaneously form a giant cubic cage with large cavity. A stoichiometric ratio (2 : 3) of **L2** and $Cd(NO_3)_2{\bullet}4H_2O$ were mixed in MeOH/$CHCl_3$ at 60°C for 2 h, followed by the addition of excess of NH_4PF_6 to give a white precipitate. After a thorough washing with water, [**$Cd_{12}L2_8$**] was isolated (90%). The related Zn^{2+}-based structure was assembled following the same procedure but using $Zn(NO_3)_2•6H_2O$ instead. Both the Cd^{2+}- and Zn^{2+}-based structures were soluble in MeCN.

The ^{1}H NMR of [**$Cd_{12}L2_8$**] (Figure 2) showed a simple pattern of the expected peaks for a tpy-metal complex. In the aromatic region, there were eight sets of aromatic protons from tpy units and phenyl groups, which were consistent with the desired structure. The protons at 6,6" position of tpy dramatically shifted upfield ($\Delta\delta$ = 0.73 ppm) due to the electron shielding effect after complexation with metal ions. The broad ^{1}H signals were indicative of a very large complex due to the slow tumbling motion on the NMR time scale.[4a] Similarly, Fujita, Nitschke and Schalley *et al.* observed broad ^{1}H signals for 3-D complexes, especially for assembles with more than 10,000 Da.[17] Note that the full assignments of ^{1}H NMR shown in Figure 1 were based on 2D-COSY (see Figure S22).The ^{13}C NMR of [**$Cd_{12}L2_8$**] showed only one series of sharp peaks due to the high symmetric architecture (see Figure S20), denoting the absence of any by-products and uncomplexed tpy moieties. HSQC spectrum was consistent with this giant cube as the sole product (see Figure S23). In DOSY (Figure 3), the observation of a distinct band at log D= -9.708 confirmed the single product formation. ^{1}H NMR pattern of [**$Zn_{12}L2_8$**] was slightly different from Cd^{2+}-based architecture (see Figure S28). Similarly, the log D = -9.725 of [**$Zn_{12}L2_8$**] observed in DOSY was close to [**$Cd_{12}L2_8$**] (Figure S29). Experimental radii of 2.9 nm and 3.0 nm were determined for [**$Cd_{12}L2_8$**] and [**$Zn_{12}L2_8$**], respectively, in close agreement with values obtained from molecular modelling (3.2 nm).

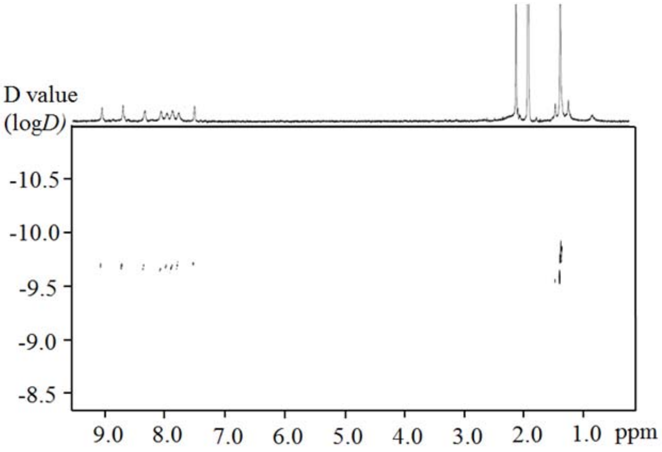


Figure 3. 2D-DOSY NMR(500 MHz) of [**$Cd_{12}L2_8$**] in CD_3CN.

Characterization by Mass Spectrometry

[**$Cd_{12}L2_8$**] and [**$Zn_{12}L2_8$**] were further characterized by ESI-MS coupled with traveling wave ion mobility-mass spectrometry (TWIM-MS)[18] to investigate the proposed structures, which have a molecular weight of 17813.6 Da and 17393.4 Da, respectively. In ESI-MS, a series of peaks with charge states from 11+ to 21+ were detected (due to the loss of a different number of counterion PF_6^-) (Figure 4A), and the isotope pattern of each peak with the corresponding simulated isotope pattern is shown in Figure S2. Notably, the isotope pattern observed for the highly charged [**$Cd_{12}L2_8$**]$^{21+}$ ion is in good accordance with the theoretical distribution (see Figure S2).

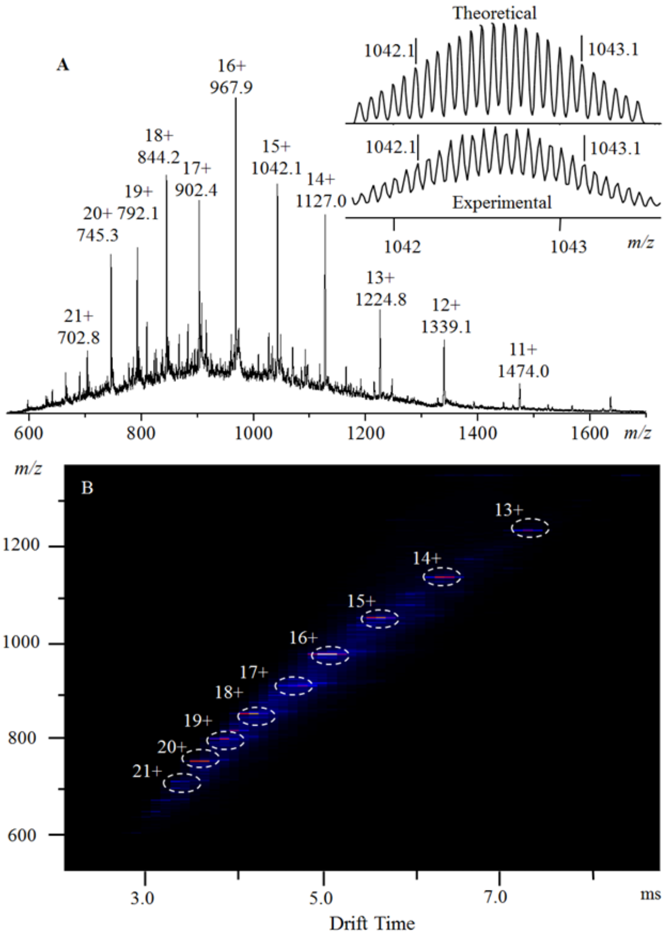


Figure 4. (A) ESI mass spectrum and (B) 2D ESI-TWIM-MS plot (*m/z* vs drift time) for [**$Cd_{12}L2_8$**].

In order to separate any superimposed fragments and examine the possible existence of overlapping isomers or conformers, TWIM-MS was used as the advanced level of MS analysis. Note that TWIM-MS provides information on the molecules' shapes and sizes based on collision cross-section (CCS), in addition to mass and compositional information.[18] As shown in Figure 4B, each charge state of the newly formed cube [**$Cd_{12}L2_8$**], for Cd^{2+}-based complexes has been detected with narrow drift time distribution, indicating the absence of other isomers or structural conformers. From the TWIM-MS data, the CCSs, which correspond to the sizes of analytes, can be calculated to provide further evidence.[19] Currently, there is no suitable metallo-supramolecular calibrants spanning the size range of the cubes under study. Therefore we used denatured proteins as calibrants for calibration, which is based on the correlation between drift time and collision cross section.[15f,16,17] Since the collision cross sections of denatured proteins were well documented, the calibration should not introduce significant deviation to experimental collision cross section calculation. The CCSs for the cubic ions in different charge states are shown in Table 1. The observed values of charges changed from 13+ to 21+ for [**$Cd_{12}L2_8$**] are consistent with a small standard deviation, *viz.*, 2809.5 ± 26.7 Å^2, suggesting these 3-D giant cubic cages are shape-persistent. In contrast, the previous study of supramolecular macrocycles showed significant differences in CCSs for different charge states, indicating the existence of different conformers due to the repulsion between charges.[18b,c,20] Thus, [**$Cd_{12}L2_8$**] and [**$Zn_{12}L2_8$**] must be more rigid and shape-persistent than macrocycles, because their structures are not twisted and their CCSs are unaffected by the charges. Similarly, Bowers and co-workers have also reported a series of rigid prism structures whose CCSs are insensitive to charge states.[21] These results clearly demonstrated TWIM-MS, as an advanced MS technique, not only probes different ions based on mass, charge and shape, but also quantitatively and accurately measures the rigidity of these species through the dependence of the CCS on the charge state.

Table 1. Experimental and Theoretical Collision Cross Sections (CCSs) of Giant Cubic Cage [**$Cd_{12}L2_8$**]

	CCS (Å^2)		
Z	exptl	expl avg	calcd avg
13+	2853.8		
14+	2804.3		
15+	2801.5		
16+	2799.0		2523.9 (5.5),[a]
17+	2849.0	2809.5 (26.7)	2797.4 (50.0),[b]
18+	2785.3		2919.8 (8.2)[c]
19+	2786.9		
20+	2823.0		
21+	2782.7		

[a] PA value obtained using MOBCAL. [b] TJ value obtained using MOBCAL. [c] EHSS value obtained using MOBCAL.

Simulation and Optical Physical Properties

All efforts to grow single crystals of [**$M_{12}L_8$**] for an X-ray diffraction study were unsuccessful, likely due to the large size and cavity with highly disordered solvent molecules and counterions. Therefore, to get a rough picture of the tetrahedron, a molecular modelling was performed to correlate the shape and size information obtained from IM-MS. Representative energy-minimized architectures were shown in Figure 4C and Figure S6. Simulation by molecular modelling agreed well with structural information calculated from TWIM-MS. Theoretical CCSs for 70 candidate structures of the [**$Cd_{12}L2_8$**] cube (obtained from molecular mechanics/dynamics simulations) were calculated using the Trajectory (TJ), projection approximation (PA) and exact hard sphere scattering (EHSS) methods.[22] There were only slight fluctuations of theoretical CCSs among these 70 candidate structures, indicating a highly rigid structure. Among them, TJ method considered both long-range interactions and momentum transfer between the ions and the gas in the ion mobility region, hence giving the most reliable CCS prediction.[22] TJ result showing theoretical CCS at 2797.4 ± 50.0 Å^2 agreed best with the average experimental CCS (*i.e.*, 2809.5 ± 26.7 Å^2) for charge states from 13+ to 21+ (Table 1), and an underestimated value (by 1%) is neglectable from the measurement errors.

Absorption and emission properties of complexes were also tested (see Figure S7-S10). The ligand **L2** in dilute $CHCl_3$ exhibited ligand-centered π-π* transitions at 296 nm. In contrast, both [**$Cd_{12}L2_8$**] and [**$Zn_{12}L2_8$**] in dilute MeCN showed two characteristic absorption peaks around 285 and 332 nm that were assigned to intra-ligand charge transfer (ILCT).[23] [**$Cd_{12}L2_8$**] and [**$Zn_{12}L2_8$**] showed photoluminescence (PL) emission around 450 nm, with an excitation wavelength of 285 nm.

Atomic Force Microscopy (AFM)

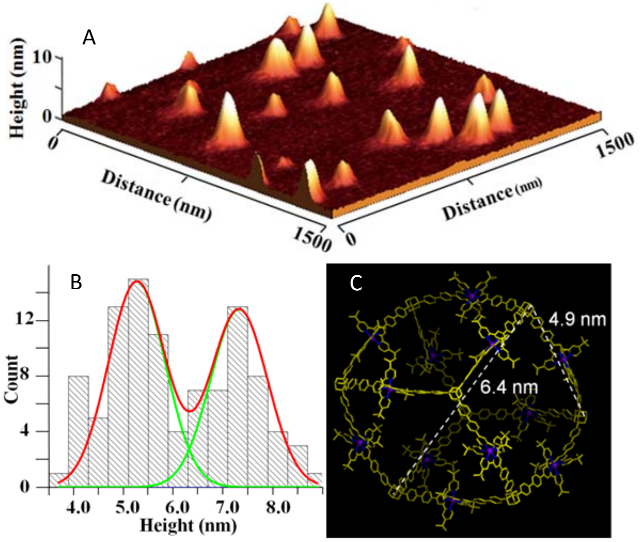


Figure 5. (A) AFM image of [**$Cd_{12}L2_8$**] on mica surface. (B) Statistical histogram of AFM for 100 particles. (C) Representative energy-minimized architecture of [**$Cd_{12}L2_8$**].

As additional evidence, the images from AFM showed the morphology of the giant cubic complex [**$Cd_{12}L2_8$**] as dots on the mica surface (Figure 5A). Some of the dots displayed cube-like shape (Figure S29). The measured height of these dots exhibited two different values: 5.22 ± 0.51 nm and 7.30 ± 0.41 nm (Figure 5B), which are close to edge length (4.9 nm) and corner-corner length (6.4 nm) shown in molecular modelling (Figure 5C), respectively. Due to the unavoidable tip broadening effect, the measured width of the dots in AFM image displayed large values.[24] Furthermore, molecular modelling shows the structure distortion of the cube is mostly neutralized by bending the two phenyl groups between adamantane and terpyridine. Therefore, the ligand bending is the major contribution to accommodate the strain. This is consistent with the bended ligand in distorted triangles as reported by other groups.[13] Finally, this giant cube with 4.9 nm edge length is significantly larger than the previously reported metallo-supramolecular cubes, which all have end-capped metal components as vertices and ligands as edges.[25]

Conclusions

In summary, we were able to employ, for the first time, terpyridine ligands as corner directing units and naked metal ions as edge gluing elements to produce giant supramolecular cubic architectures. By carefully design of the arm length versus its mutual angle, the structurally controlled cubic cages have been prepared stoichiometrically from complementary 2,2':6',2"-terpyridine ligands and metal ions. To the best of our knowledge, these are hitherto the largest cubic shape self-assemblies. DOSY NMR and AFM prove the remarkable size of cube. TWIM-MS unambiguously measures the molecular weight and elemental compositions, and provides profound insight into the particles' shapes, sizes, and the rigidity of the complexes. Through changing the length, angle and rigidity of adamantane-based terpyridine ligand, we may obtain discrete trigonal bipyramidal like dimer (**M_3L_2**), tetrahedron (**M_6L_4**) and dodecahedron (**$M_{30}L_{20}$**) from Platonic solids in the future study. More importantly, this series of 3-D architectures with different sizes of internal cavities and face windows may become an ideal system for host-guest chemistry study.

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Notes and references

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1 (a) Wikoff, W. R.; Liljas, L.; Duda, R. L.; Tsuruta, H.; Hendrix, R. W.; Johnson, J. E. *Science* **2000**, *289*, 2129; (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) Pornillos, O.; Ganser-Pornillos, B. K.; Kelly, B. N.; Hua, Y.; Whitby, F. G.; Stout, C. D.; Sundquist, W. I.; Hill, C. P.; Yeager, M. *Cell* **2009**, *137*, 1282.

2 (a) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Leize, E.; Van Dorsselaer, A. *Angew. Chem. Int. Ed.* **1998**, *37*, 3265; (b) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem. Int. Ed.* **1996**, *35*, 1838; (c) Lehn, J.-M. *Chem. Soc. Rev.* **2007**, *36*, 151.

3 (a) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810; (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369; (c) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. *Coord. Chem. Rev.* **2008**, *252*, 825.

4 For recent examples, see: (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) 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; (c) Hastings, C. J.; Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 6938; (d) Chepelin, O.; Ujma, J.; Wu, X.; Slawin, A. M. Z.; Pitak, M. B.; Coles, S. J.; Michel, J.; Jones, A. C.; Barran, P. E.; Lusby, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 19334; (e) Freye, S.; Hey, J.; Torras-Galán, A.; Stalke, D.; Herbst-Irmer, R.; John, M.; Clever, G. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 2191; (f) Meng, W.; Ronson, T. K.; Nitschke, J. R. *Proc. Natl. Acad. Sci. USA.* **2013**, *110*, 10531; (g) Sanchez-Molina, I.; Grimm, B.; Krick Calderon, R. M.; Claessens, C. G.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2013**, *135*, 10503; (h) Shanmugaraju, S.; Jadhav, H.; Patil, Y. P.; Mukherjee, P. S. *Inorg. Chem.* **2012**, *51*, 13072; (i) Clever, G. H.; Tashiro, S.; Shionoya, M. *J. Am. Chem. Soc.* **2010**, *132*, 9973; (j) Hiraoka, S.; Yamauchi, Y.; Arakane, R.; Shionoya, M. *J. Am. Chem. Soc.* **2009**, *131*, 11646; (k) Samanta, D.; Mukherjee, S.; Patil, Y. P.; Mukherjee, P. S. *Chem. Eur. J.* **2012**, *18*, 12322; (l) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J. *Org. Lett.* **2002**, *4*, 913; (m) Kryschenko, Y. K.; Seidel, S. R.; Muddiman, D. C.; Nepomuceno, A. I.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 9647; (n) Bilbeisi, R. A.; Ronson, T. K.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 9027.

5 (a) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251. (b) Hastings, C. J.; Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 6938.

6 (a) Kikuchi, T.; Murase, T.; Sato, S.; Fujita, M. *Supramol. Chem.* **2008**, *20*, 81; (b) Suzuki, K.; Takao, K.; Sato, S.; Fujita, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 4858; (c) Takao, K.; Suzuki, K.; Ichijo, T.; Sato, S.; Asakura, H.; Teramura, K.; Kato, K.; Ohba, T.; Morita, T.; Fujita, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 5893.

7 (a) Sørensen, A.; Castilla, A. M.; Ronson, T. K.; Pittelkow, M.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 11273; (b) Bolliger, J. L.; Belenguer, A. M.; Nitschke, J. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 7958; (c) Smulders, M. M. J.; Zarra, S.; Nitschke, J. R. *J. Am. Chem. Soc.* **2013**, *135*, 7039; (d) Riddell, I. A.; Smulders, M. M. J.; Clegg, J. K.; Nitschke, J. R. *Chem. Commun.* **2011**, *47*, 457; (e) Schalley, C. A.; Lützen, A.; Albrecht, M. *Chem. Eur. J.* **2004**, *10*, 1072. (f) Mahata, K,; Frischmann, P. D.; Würthner, F. *J. Am. Chem. Soc*. **2013**, *135*, 15656.

8 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.

9 (a) Wild, A.; Winter, A.; Schlutter, F.; Schubert, U. S. *Chem. Soc. Rev.* **2011**, *40*, 1459; (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem. Int. Ed.* **2002**, *41*, 2892; (c) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373. (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.

10 (a) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Baker, G. R.; Cush, R.; Russo, P. S. *Angew. Chem. Int. Ed*. **1999**, *38*, 3717; (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) Constable, E. C.; Dunphy, E. L.; Housecroft, C. E.; Kylberg, W.; Neuburger, M.; Schaffner, S.; Schofield,a E. R.; Smith, C. B. *Chem. Eur. J*. **2006**, *12*, 4600; (d) Winter, A.; Friebe, C.; Chiper, M.; Hager M. D.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem*. **2009**, *47*, 4083; (e) Siebert, R.; Tian, Y.; Camacho, R.; Winter, A.; Wild, A.; Krieg, A.; Schubert, U. S.; Popp, J.; Scheblykin, I. G.; Dietzek, B. *J. Mater. Chem*. **2012**, *22*, 16041; (f) Kotova, O.; Daly, R.; Santos C. M.; Boese, M.; Kruger, P. E.; Boland, J. J.; Gunnlaugsson, T. *Angew. Chem. Int. Ed*. **2012**, *51*, 7208; (g) Leung, S. Y.; Lam, W. H.; Yam, V. W. *Proc. Natl. Acad. Sci. USA*. **2013**, *110*, 7986; (h) Yeunga, M. C.; Yam, V. W. *Chem. Sci*., **2013**, *4*, 2928; (i) Wild, A.; Winter, A.; Hager, M. D.; Görls, H.; Schubert, U. S. *Marcromol. Rapid Commun*. **2012**, *33*, 517.

11 (a) Schröder, T.; Brodbeck, R.; Letzel, M. C.; Mix, A.; Schnatwinkel, B.; Tonigold, M.; Volkmer, D.; Mattay, J. *Tetrahedron Lett*. **2008**, *49*, 5939; (b) S. Cardona-Serra, E. Coronado, P. Gavina, J. Ponce, S. Tatay, *Chem. Commun*. **2011**, *47*, 8235; (c) M. Schmittel, B. He, *Chem. Commun*. 2008, 4723; (d) M. Schmittel, B. He, P. Mal, *Org. Lett*. **2008**, *10*, 2513.

12 Torquato, S.; Jiao, Y. *Nature* **2009**, *460*, 876.

13 (a) Weilandt, T.; Troff, R. W.; Saxell, H.; Rissanen, K.; Schalley, C. A. *Inorg. Chem*. **2008**, *47*, 7588; (b) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun*. **1996**, 1535.

14 Fujita, D.; Takahashi, A.; Sato, S.; Fujita, M. *J. Am. Chem. Soc*. **2011**, *133*, 13317.

15 Newman, H. *Synthesis* **1972**, *1972*, 692.

16 Chin, D. N.; Gordon, D. M.; Whitesides, G. M. *J. Am. Chem. Soc*. **1994**, *116*, 12033.

17 (a) Sun, Q. F.; Sato, S.; Fujita, M. *Nat. Chem*. **2012**, *4*, 330; (b) Sun, Q.-F.; Murase, T.; Sato, S.; Fujita, M. *Angew. Chem. Int. Ed*. **2011**, *50*, 10318; (c) Bunzen, J.; Iwasa, J.; Bonakdarzadeh, P.; Numata, E.; Rissanen, K.; Sato, S.; Fujita, M. *Angew. Chem. Int. Ed*. **2012**, *51*, 3161; (d) 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.

18 (a) Li, X.; Chan, Y.-T.; Newkome, G. R.; Wesdemiotis, C. *Anal. Chem*. **2011**, *83*, 1284; (b) Wang, J.-L.; Li, X.; Lu, X.; Chan, Y.-T.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Eur. J*. **2011**, *17*, 4830; (c) Chan, Y.-T.; Li, X.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Eur. J*. **2011**, *17*, 7750; (d) 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; (e) 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; (f) Scarff, C. A.; Snelling, J. R.; Knust, M. M.; Wilkins, C. L.; Scrivens, J. H. *J. Am. Chem. Soc*. **2012**, *134*, 9193.

19 Thalassinos, K.; Grabenauer, M.; Slade, S. E.; Hilton, G. R.; Bowers, M. T.; Scrivens, J. H. *Anal. Chem*. **2008**, *81*, 248.

20 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.

21 Brocker, E. R.; Anderson, S. E.; Northrop, B. H.; Stang, P. J.; Bowers, M. T. *J. Am. Chem. Soc*. **2010**, *132*, 13486.

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

23 Bugarin, A.; Connell, B. T. *Organometallics* **2008**, *27*, 4357.

24 (a) Radmacher, M.; Fritz, M.; Hansma, H.; Hansma, P. *Science* **1994**, *265*, 1577; (b) Chen, G.; Zhou, J.; Park, B.; Xu, B. *Appl. Phys. Lett*. **2009**, *95*, 043103; (c) Ichijo, T.; Sato, S.; Fujita, M. *J. Am. Chem. Soc*. **2013**, *135*, 6786.

25 (a) Klausmeyer, K. K.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem. Int. Ed*. **1998**, *37*, 1694; (b) Wang, M.; Zheng, Y.-R.; Cook, T. R.; Stang, P. J. *Inorg. Chem*. **2011**, *50*, 6107; (c) Wang, M.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. *J. Am. Chem. Soc*. **2010**, *132*, 6282; (d) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc*. **1999**, *121*, 2705; (e) Contakes, S. M.; Klausmeyer, K. K.; Milberg, R. M.; Wilson, S. R.; Rauchfuss, T. B. *Organometallics* **1998**, *17*, 3633; (f) Roche, S.; Haslam, C.; L. Heath, S.; A. Thomas, J. *Chem. Commun*. **1998**, 1681. (o) 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.