Chemical Science

EDGE ARTICLE



View Article Online

Cite this: Chem. Sci., 2014, 5, 1221

Received 26th October 2013 Accepted 21st November 2013

DOI: 10.1039/c3sc52965g

www.rsc.org/chemicalscience

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(n) and Pd(n)-mediated self-assembly with pyridyl ligands, the coordination geometry of the metal ions and angle of ligands plays a vital role 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

^aDepartment of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666, USA. E-mail: X_L8@txstate.edu; M_W134@txstate.edu

‡ These authors contributed equally.

Self-assembly of giant supramolecular cubes with terpyridine ligands as vertices and metals on edges[†]

Chao Wang,‡^a Xin-Qi Hao,‡^b Ming Wang,^{*a} Cunlan Guo,^c Bingqian Xu,^c Eric N. Tan,^a Yan-Yan Zhang,^d Yihua Yu,^d Zhong-Yu Li,^e Hai-Bo Yang,^e Mao-Ping Song^b and Xiaopeng Li^{*a}

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 18 k 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 [$M_{12}L_8$] 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, travelling wave ion mobility-MS and AFM.

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- $M(\pi)$ -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 synthesis6 and guest encapsulation.7

A strategic design with coordination-driven self-assembly of the supramolecular cube $[M_{12}L_8]$ (Fig. 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

^bCollege of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, P. R. China

^cSingle Molecule Study Laboratory, College of Engineering and Nanoscale Science and Engineering Center, University of Georgia, Athens, GA 30602, USA

^dShanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, P. R. China

^eShanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, P. R. China

[†] Electronic supplementary information (ESI) available: Synthetic procedure, characterization data (NMR, ESI-MS, UV-vis, PL, AFM) for the cubic cages and details of CCS calculations and molecular simulations. See DOI: 10.1039/c3sc52965g



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



 $\label{eq:scheme1} Scheme 1 \quad \mbox{Synthetic route to the ligands and } [M_{12}L_8].$

ligand was designed by incorporating three tpy groups into rigid adamantane core, which provides 109°28' geometry based on sp³ hybridization at its points of bisection. When the threearmed 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 $109^{\circ}28'$ 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 to 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 hypothesize that these symmetric cubic cages would be more thermodynamically stable than other assembles (*e.g.*, dodecahedron) if an appropriate length of linker between adamantane and terpyridine was applied.

Results and discussion

Synthetic procedures

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 Zn₁₂L1₈ composition was observed by ESI-MS (see Fig. 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 Fig. 1 is mainly because of the low intensity of signal due to the low solubility of $M_{12}L1_8$ and the encapsulation of solvent or salt molecules inside the cube.

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 ¹H NMR was easily discernible compared to the ligand without *t*-butyl groups (see ESI[†]). Ligand **L2** was fully characterized by NMR and ESI-MS. In the aromatic region of ¹H NMR (Fig. 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.

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(NO₃)₂·4H₂O were mixed in MeOH–CHCl₃ at 60 °C for 2 h, followed by the addition of excess of NH₄PF₆ to give a white precipitate. After a thorough washing with water, [Cd₁₂L2₈] was isolated (90%). The related Zn²⁺-based structure was assembled following the same procedure but using Zn(NO₃)₂·6H₂O instead. Both the Cd²⁺- and Zn²⁺-based structure wase were soluble in MeCN.



Fig. 2 1 H NMR spectra (400 MHz) of ligand L2 in CDCl₃ and [Cd₁₂L2₈] in CD₃CN.

The ¹H NMR of $[Cd_{12}L2_8]$ (Fig. 2) shows 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 ¹H 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 ¹H signals for 3-D complexes, especially for assembles with more than 10 000 Da.¹⁷ Note that the full assignments of ¹H NMR shown in Fig. 1 are based on 2D-COSY (see Fig. S22[†]). The ¹³C NMR of [Cd₁₂L2₈] showed only one series of sharp peaks due to the high symmetric architecture (see Fig. 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 Fig. S23[†]). In DOSY (Fig. 3), the observation of a distinct band at $\log D = -9.708$ confirmed the single product formation. ¹H NMR pattern of $[Zn_{12}L2_8]$ was slightly different from Cd²⁺-based architectures (see Fig. S28[†]). Similarly, the log D = -9.725 of $[\mathbf{Zn}_{12}\mathbf{L2}_8]$



Fig. 3 2D-DOSY NMR (500 MHz) of [Cd₁₂L2₈] in CD₃CN.

observed in DOSY was close to $[Cd_{12}L2_8]$ (Fig. 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).

Characterization by mass spectrometry

 $[Cd_{12}L2_8]$ and $[Zn_{12}L2_8]$ were further characterized by ESI-MS coupled with travelling 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^-) (Fig. 4A), and the isotope pattern of each peak with the corresponding simulated isotope pattern is shown in Fig. 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 Fig. S2†).

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 Fig. 4B, each charged state of the newly formed cube



Fig. 4 (A) ESI mass spectrum and (B) 2D ESI-TWIM-MS plot (m/z vs. drift time) for [Cd₁₂L2₈].

[Cd₁₂L2₈], for Cd²⁺-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.15-17 Since the collision cross sections of denatured proteins were well documented, the calibration should not introduce significant deviation to experimental collision cross section calculations. 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 \pm 26.7 Å², suggesting these 3-D giant cubic cages are shape-persistent. In contrast, the previous study of supramolecular macrocycles shows significant differences in CCSs for different charge states, indicating the existence of different conformers due to the repulsion between charges.18b,c,20 Thus, [Cd12L28] and [Zn12L28] 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 demonstrate TWIM-MS, as an advanced MS technique, not only probing different ions based on mass, charge and shape, but also quantitatively and accurately measuring the rigidity of these species through the dependence of the CCS on the charge state.

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, molecular modelling was performed to correlate the shape and size information obtained from IM-MS. Representative energy-minimized architectures are shown in Fig. 4C and S6.†

Table 1 Experimental and theoretical Collision Cross Sections (CCSs) of giant cubic cage $[Cd_{12}L2_8]$

Z	CCS (Å ²)		
	Exptl	Exptl avg	Calcd avg
13+	2853.8	2809.5 (26.7)	2523.9 (5.5), ^a
14+	2804.3		2797.4 (50.0), ^b
15+	2801.5		$2919.8 (8.2)^{c}$
16+	2799.0		
17+	2849.0		
18+	2785.3		
19+	2786.9		
20+	2823.0		
21+	2782.7		
21+	2/82./		

^{*a*} PA value obtained using MOBCAL. ^{*b*} TJ value obtained using MOBCAL. ^{*c*} EHSS value obtained using MOBCAL.

Simulation by molecular modelling agreed well with structural information calculated from TWIM-MS. Theoretical CCSs for 70 candidate structures of the [Cd12L28] 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 \pm 50.0 ${\rm \AA}^2$ agreed best with the average experimental CCS (i.e., 2809.5 \pm 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 Fig. S7–S10†). The ligand L2 in dilute CHCl₃ exhibited ligand-centered π – π * transitions at 296 nm. In contrast, both [Cd₁₂L2₈] and [Zn₁₂L2₈] in dilute MeCN showed two characteristic absorption peaks around 285 and 332 nm that were assigned to intra-ligand charge transfer (ILCT).²³ [Cd₁₂L2₈] and [Zn₁₂L2₈] showed photoluminescence (PL) emission around 450 nm, with an excitation wavelength of 285 nm.

Atomic force microscopy (AFM)

As additional evidence, the images from AFM show the morphology of the giant cubic complex $[Cd_{12}L2_8]$ as dots on the mica surface (Fig. 5A). Some of the dots displayed cube-like shape (Fig. S29†). The measured height of these dots exhibited two different values: 5.22 ± 0.51 nm and 7.30 ± 0.41 nm (Fig. 5B), which are close to edge length (4.9 nm) and corner-corner length (6.4 nm) shown in molecular modelling (Fig. 5C), respectively. Due to the unavoidable tip broadening effect, the



Fig. 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 $[Cd_{12}L2_8]$.

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 careful 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.

Acknowledgements

X. L. gratefully acknowledges the support from the Research Enhancement Program of Texas State University, the Welch Foundation (AI-0045), and the REU support from NSF (CHE-1156579) to Eric N. Tan. X.-Q. H. thanks the NSFC/China (no. 21102135) for financial support. H.-B. Y. thanks the NSFC/ China (no. 21132005 and 91027005) and the SMSTC (no. 13JC1402200) for financial support.

Notes and references

- (a) W. R. Wikoff, L. Liljas, R. L. Duda, H. Tsuruta, R. W. Hendrix and J. E. Johnson, *Science*, 2000, 289, 2129;
 (b) M. Rappas, J. Schumacher, F. Beuron, H. Niwa, P. Bordes, S. Wigneshweraraj, C. A. Keetch, C. V. Robinson, M. Buck and X. Zhang, *Science*, 2005, 307, 1972; (c)
 O. Pornillos, B. K. Ganser-Pornillos, B. N. Kelly, Y. Hua, F. G. Whitby, C. D. Stout, W. I. Sundquist, C. P. Hill and M. Yeager, *Cell*, 2009, 137, 1282.
- 2 (a) B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize and A. Van Dorsselaer, *Angew. Chem., Int. Ed.*, 1998, 37, 3265; (b)
 B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum and

D. Fenske, Angew. Chem., Int. Ed., 1996, 35, 1838; (c) J.-M. Lehn, Chem. Soc. Rev., 2007, 36, 151.

- 3 (a) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, 111, 6810; (b) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, 38, 369; (c) S. J. Dalgarno, N. P. Power and J. L. Atwood, *Coord. Chem. Rev.*, 2008, 252, 825.
- 4 For recent examples, see: (a) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, Science, 2010, 328, 1144; (b) Y.-R. Zheng, Z. Zhao, M. Wang, K. Ghosh, J. B. Pollock, T. R. Cook and P. J. Stang, J. Am. Chem. Soc., 2010, 132, 16873; (c) C. J. Hastings, M. D. Pluth, R. G. Bergman and K. N. Raymond, J. Am. Chem. Soc., 2010, 132, 6938; (d) O. Chepelin, J. Ujma, X. Wu, A. M. Z. Slawin, M. B. Pitak, S. J. Coles, J. Michel, A. C. Jones, P. E. Barran and P. J. Lusby, J. Am. Chem. Soc., 2012, 134, 19334; (e) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John and G. H. Clever, Angew. Chem., Int. Ed., 2012, 51, 2191; (f) W. Meng, T. K. Ronson and J. R. Nitschke, Proc. Natl. Acad. Sci. U. S. A., 2013, 110, 10531; (g) I. Sanchez-Molina, B. Grimm, R. M. Krick Calderon, C. G. Claessens, D. M. Guldi and T. J. Torres, J. Am. Chem. Soc., 2013, 135, 10503; (h) S. Shanmugaraju, H. Jadhav, Y. P. Patil and P. S. Mukherjee, Inorg. Chem., 2012, 51, 13072; (i) G. H. Clever, S. Tashiro and M. Shionoya, J. Am. Chem. Soc., 2010, 132, 9973; (j) S. Hiraoka, Y. Yamauchi, R. Arakane and M. Shionoya, J. Am. Chem. Soc., 2009, 131, 11646; (k) D. Samanta, S. Mukherjee, Y. P. Patil and P. S. Mukherjee, Chem.-Eur. J., 2012, 18, 12322; (1) C. J. Kuehl, T. Yamamoto, S. R. Seidel and P. J. Stang, Org. Lett., 2002, 4, 913; (m) Y. K. Kryschenko, S. R. Seidel, D. C. Muddiman, A. I. Nepomuceno and P. J. Stang, J. Am. Chem. Soc., 2003, 125, 9647; (n) R. A. Bilbeisi, T. K. Ronson and J. R. Nitschke, Angew. Chem., Int. Ed., 2013, 52, 9027.
- 5 (a) M. Yoshizawa, M. Tamura and M. Fujita, Science, 2006,
 312, 251; (b) C. J. Hastings, M. D. Pluth, R. G. Bergman and K. N. Raymond, J. Am. Chem. Soc., 2010, 132, 6938.
- 6 (a) T. Kikuchi, T. Murase, S. Sato and M. Fujita, Supramol. Chem., 2008, 20, 81; (b) K. Suzuki, K. Takao, S. Sato and M. Fujita, Angew. Chem., Int. Ed., 2011, 50, 4858; (c)
 K. Takao, K. Suzuki, T. Ichijo, S. Sato, H. Asakura, K. Teramura, K. Kato, T. Ohba, T. Morita and M. Fujita, Angew. Chem., Int. Ed., 2012, 51, 5893.
- 7 (a) A. Sørensen, A. M. Castilla, T. K. Ronson, M. Pittelkow and J. R. Nitschke, Angew. Chem., Int. Ed., 2013, 52, 11273;
 (b) J. L. Bolliger, A. M. Belenguer and J. R. Nitschke, Angew. Chem., Int. Ed., 2013, 52, 7958; (c) M. M. J. Smulders, S. Zarra and J. R. Nitschke, J. Am. Chem. Soc., 2013, 135, 7039; (d) I. A. Riddell, M. M. J. Smulders, J. K. Clegg and J. R. Nitschke, Chem. Commun., 2011, 47, 457; (e) C. A. Schalley, A. Lützen and M. Albrecht, Chem.-Eur. J., 2004, 10, 1072; (f) K. Mahata, P. D. Frischmann and F. Würthner, J. Am. Chem. Soc., 2013, 135, 15656.
- 8 D. Fujita, K. Suzuki, S. Sato, M. Yagi-Utsumi, Y. Yamaguchi, N. Mizuno, T. Kumasaka, M. Takata, M. Noda, S. Uchiyama, K. Kato and M. Fujita, *Nat. Commun.*, 2012, **3**, 1093.

- 9 (a) A. Wild, A. Winter, F. Schlutter and U. S. Schubert, *Chem. Soc. Rev.*, 2011, 40, 1459; (b) U. S. Schubert and C. Eschbaumer, *Angew. Chem., Int. Ed.*, 2002, 41, 2892; (c) H. Hofmeier and U. S. Schubert, *Chem. Soc. Rev.*, 2004, 33, 373; (d) E. C. Constable, *Chem. Soc. Rev.*, 2007, 36, 246; (e) E. C. Constable, *Coord. Chem. Rev.*, 2008, 252, 842; (f) S. De, K. Mahata and M. Schmittel, *Chem. Soc. Rev.*, 2010, 39, 1555.
- 10 (a) G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush and P. S. Russo, Angew. Chem., Int. Ed., 1999, 38, 3717; (b) J.-L. Wang, X. Li, X. Lu, I. F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng and G. R. Newkome, J. Am. Chem. Soc., 2011, 133, 11450; (c) E. C. Constable, E. L. Dunphy, C. E. Housecroft, W. Kylberg, M. Neuburger, S. Schaffner, a. E. R. Schofield and C. B. Smith, Chem.-Eur. J., 2006, 12, 4600; (d) A. Winter, C. Friebe, M. Chiper, M. D. Hager and U. S. Schubert, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 4083; (e) R. Siebert, Y. Tian, R. Camacho, A. Winter, A. Wild, A. Krieg, U. S. Schubert, J. Popp, I. G. Scheblykin and B. Dietzek, J. Mater. Chem., 2012, 22, 16041; (f) O. Kotova, R. Daly, C. M. Santos, M. Boese, P. E. Kruger, J. J. Boland and T. Gunnlaugsson, Angew. Chem., Int. Ed., 2012, 51, 7208; (g) S. Y. Leung, W. H. Lam and V. W. Yam, Proc. Natl. Acad. Sci. U. S. A., 2013, 110, 7986; (h) M. C. Yeunga and V. W. Yam, Chem. Sci., 2013, 4, 2928; (i) A. Wild, A. Winter, M. D. Hager, H. Görls and U. S. Schubert, Macromol. Rapid Commun., 2012, 33, 517.
- 11 (a) T. Schröder, R. Brodbeck, M. C. Letzel, A. Mix, B. Schnatwinkel, M. Tonigold, D. Volkmer and J. Mattay, *Tetrahedron Lett.*, 2008, 49, 5939; (b) S. Cardona-Serra, E. Coronado, P. Gavina, J. Ponce and S. Tatay, *Chem. Commun.*, 2011, 47, 8235; (c) M. Schmittel and B. He, *Chem. Commun.*, 2008, 4723; (d) M. Schmittel, B. He and P. Mal, *Org. Lett.*, 2008, 10, 2513.
- 12 S. Torquato and Y. Jiao, Nature, 2009, 460, 876.
- 13 (a) T. Weilandt, R. W. Troff, H. Saxell, K. Rissanen and C. A. Schalley, *Inorg. Chem.*, 2008, 47, 7588; (b) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535.
- 14 D. Fujita, A. Takahashi, S. Sato and M. Fujita, *J. Am. Chem. Soc.*, 2011, **133**, 13317.
- 15 H. Newman, Synthesis, 1972, 1972, 692.
- 16 D. N. Chin, D. M. Gordon and G. M. Whitesides, J. Am. Chem. Soc., 1994, 116, 12033.
- 17 (a) Q. F. Sun, S. Sato and M. Fujita, *Nat. Chem.*, 2012, 4, 330;
 (b) Q.-F. Sun, T. Murase, S. Sato and M. Fujita, *Angew. Chem.*, *Int. Ed.*, 2011, 50, 10318; (c) J. Bunzen, J. Iwasa,

P. Bonakdarzadeh, E. Numata, K. Rissanen, S. Sato and M. Fujita, *Angew. Chem., Int. Ed.*, 2012, **51**, 3161; (*d*) S. P. Black, A. R. Stefankiewicz, M. M. J. Smulders, D. Sattler, C. A. Schalley, J. R. Nitschke and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2013, **52**, 5749.

- 18 (a) X. Li, Y.-T. Chan, G. R. Newkome and C. Wesdemiotis, Anal. Chem., 2011, 83, 1284; (b) J.-L. Wang, X. Li, X. Lu, Y.-T. Chan, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, Chem.-Eur. J., 2011, 17, 4830; (c) Y.-T. Chan, X. Li, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, Chem.-Eur. J., 2011, 17, 7750; (d) J. Ujma, M. De Cecco, O. Chepelin, H. Levene, C. Moffat, S. J. Pike, P. J. Lusby and P. E. Barran, Chem. Commun., 2012, 48, 4423; (e) J. Thiel, D. Yang, M. H. Rosnes, X. Liu, C. Yvon, S. E. Kelly, Y.-F. Song, D.-L. Long and L. Cronin, Angew. Chem., Int. Ed., 2011, 50, 8871; (f) C. A. Scarff, J. R. Snelling, M. M. Knust, C. L. Wilkins and J. H. Scrivens, J. Am. Chem. Soc., 2012, 134, 9193.
- 19 K. Thalassinos, M. Grabenauer, S. E. Slade, G. R. Hilton, M. T. Bowers and J. H. Scrivens, *Anal. Chem.*, 2008, **81**, 248.
- 20 Y.-T. Chan, X. Li, J. Yu, G. A. Carri, C. N. Moorefield, G. R. Newkome and C. Wesdemiotis, *J. Am. Chem. Soc.*, 2011, 133, 11967.
- 21 E. R. Brocker, S. E. Anderson, B. H. Northrop, P. J. Stang and M. T. Bowers, J. Am. Chem. Soc., 2010, 132, 13486.
- 22 (a) A. A. Shvartsburg and M. F. Jarrold, *Chem. Phys. Lett.*, 1996, 261, 86; (b) M. F. Jarrold, *Annu. Rev. Phys. Chem.*, 2000, 51, 179; (c) A. A. Shvartsburg, B. Liu, K. W. M. Siu and K.-M. Ho, *J. Phys. Chem. A*, 2000, 104, 6152.
- 23 A. Bugarin and B. T. Connell, *Organometallics*, 2008, 27, 4357.
- 24 (a) M. Radmacher, M. Fritz, H. Hansma and P. Hansma, *Science*, 1994, 265, 1577; (b) G. Chen, J. Zhou, B. Park and B. Xu, *Appl. Phys. Lett.*, 2009, 95, 043103; (c) T. Ichijo, S. Sato and M. Fujita, *J. Am. Chem. Soc.*, 2013, 135, 6786.
- 25 (a) K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, Angew. Chem., Int. Ed., 1998, 37, 1694; (b) M. Wang, Y.-R. Zheng, T. R. Cook and P. J. Stang, Inorg. Chem., 2011, 50, 6107; (c) M. Wang, Y.-R. Zheng, K. Ghosh and P. J. Stang, J. Am. Chem. Soc., 2010, 132, 6282; (d) K. K. Klausmeyer, S. R. Wilson and T. B. Rauchfuss, J. Am. Chem. Soc., 1999, 121, 2705; (e) S. M. Contakes, K. K. Klausmeyer, R. M. Milberg, S. R. Wilson and T. B. Rauchfuss, Organometallics, 1998, 17, 3633; (f) S. Roche, C. Haslam, L. S. Heath and J. A. Thomas, Chem. Commun., 1998, 1681; (g) I. S. Tidmarsh, T. B. Faust, H. Adams, L. P. Harding, L. Russo, W. Clegg and M. D. Ward, J. Am. Chem. Soc., 2008, 130, 15167.