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Metal ion-modulated self-assembly of pseudo-suit[3]anes using crown ether-based terpyridine metalloprisms†

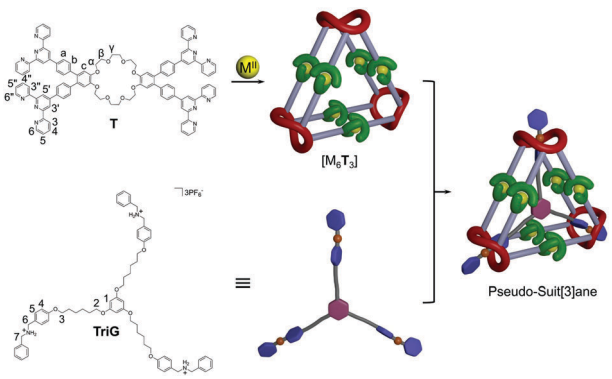
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Two hexanuclear metalloprisms possessing three dibenzo[24]crown-8 units were generated in quantitative yields by complexation of the predesigned tetratopic 2,2′:6′,2″-terpyridine ligand (T) with Cd^{II} and Zn^{II} ions, respectively. The prismatic hosts were subsequently self-assembled with the trifunctional guest molecule (TriG) containing dibenzylammonium ions to afford the corresponding metallo-supramolecular pseudo-suit[3]anes. It was serendipitously found that the host–guest inclusion rates could be modulated by the subtle dynamic difference in metal–ligand frameworks, finally leading to a selective encapsulation event in the presence of both metallo-suits.

Based on lessons from nature,[1] scientists have endeavored to understand the underlying principles of molecular assembly for construction of well-defined functional nanoobjects.[2] One of the most attractive aspects is to investigate their dynamic features.[3] To this end, a variety of synthetic strategies have been developed to prepare mechanically interlocked molecules.[4] Among them, the internally stoppered suit[*n*]anes (*n* = 2 and 3) have been elegantly constructed by template-directed synthesis relying on dynamic imine bonds and the binding of dialkylammonium ions with dipyrido[24]crown-8.[5] Nevertheless, expanding the scope of suitane-type motifs still remains a synthetic challenge. To explore facile construction approaches, other combinations of directional secondary interactions might be considered.

Over the past two decades, metal coordination-driven self-assembly has been widely utilized in the preparation of designable supramolecular topologies.[6] Besides, several examples have demonstrated that coordination bonds have high tolerance to other noncovalent interactions during self-assembly.[7] For instance, a series of multivalent hosts have been prepared through the coordination of crown ether-functionalized terpyridine ligands with metal ions, and then used for the assembly of pseudo-rotaxanes.[7h] Herein, we examine the orthogonality between metal–ligand coordination bonds and ion–dipole interactions in our predesigned building blocks. Two prismatic metallocages bearing crown ethers are readily constructed in quantitative yields, and further assembled into metallo-supramolecular pseudo-suit[3]anes with a trifunctional guest molecule. Through kinetic control, the dynamic discrepancy of the metal–ligand frameworks results in a selective host–guest inclusion process.

Very recently, various metallo-supramolecular polyhedra self-assembled from multitopic terpyridine ligands and Zn^{II} ions have been well documented.[8] Using a similar design principle, ligand **T** (Scheme 1) containing dibenzo[24]crown-8 (DB24C8) was synthesized in two steps (Scheme S1, ESI†). Treatment of DB24C8 with NBS in THF yielded the tetrabrominated product, which was followed by the Suzuki–Miyaura coupling reaction with 4′-(4-boronophenyl)–tpy (where tpy = 2,2′:6′,2″-terpyridine) to generate the tetratopic ligand in good yield (82%). To explore the self-assembly behavior of the crown ether-based tetrakis(terpyridine), **T** was treated with 2 equivalents of $Cd(NO_3)_2{\cdot}4H_2O$ in a mixed solvent of MeOH and $CHCl_3$ (1 : 1, v/v). After the mixture was stirred at 25 °C for 30 min, excess NH_4PF_6 (20 equiv. of NO_3^-) was added to precipitate the Cd^{II} complex with PF_6^- as counterions in quantitative yield. The Zn^{II} complex was



Scheme 1 Chemical structures of ligand **T** and trifunctional guest **TriG**, and self-assembly of a metallo-supramolecular pseudo-suit[3]ane.

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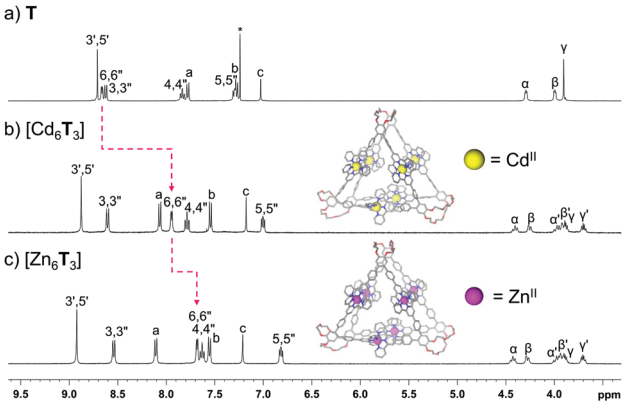


Fig. 1 ^{1}H NMR spectra of (a) **T**, (b) [Cd_6**T**$_3$], and (c) [Zn_6**T**$_3$]. The signal of $CHCl_3$ is denoted by an asterisk.

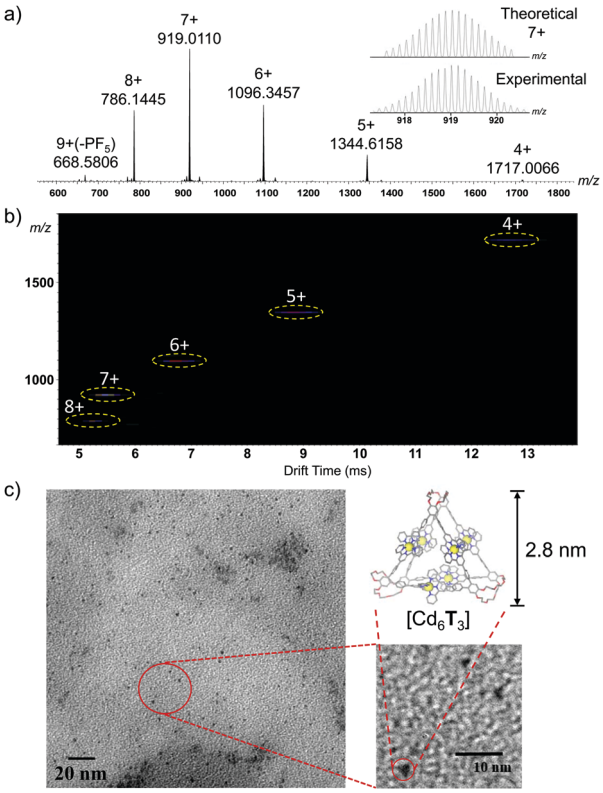


Fig. 2 (a) ESI-MS spectrum, (b) ESI-TWIM-MS plot, and (c) TEM micrographs and energy-minimized geometry of [Cd_6**T**$_3$].

obtained in a similar manner after stirring at 70 °C for 3 days (see the ESI†).

The ^{1}H NMR spectra of Cd^{II} and Zn^{II} complexes exhibited one set of sharp and well-resolved peaks (Fig. 1b and c) for the tpy motifs, and the characteristic upfield shifts for the doublets assigned to the 6,6″-tpy protons indicated the formation of an octahedral complex $\langle M^{II}\rangle$ (where <= tpy and M = Cd or Zn).[9] The proper assignments were further confirmed by ^{1}H COSY NMR (Fig. S4 and S6, ESI†). Notably, the ^{1}H NMR peak splitting for the ethylene oxide units was clearly observed in either case. It can be rationalized that when a discrete polyhedron was formed by **T**, the conformational flexibility of the ethylene oxide units was restricted, and the locked conformation led to a split into two different proton resonances as compared to the uncoordinated ligand. The existence of a single self-assembled species in CD_3CN was evident from the DOSY spectra (Fig. S5 and S7, ESI†). The assembled compositions of [Cd_6**T**$_3$] and [Zn_6**T**$_3$] were verified by the ESI-MS spectra (Fig. 2a and Fig. S9, ESI†) that revealed a series of peaks attributed to the ions derived from the combination of 3 ligands, 6 metal ions (Cd^{II} or Zn^{II}), and the corresponding number of PF_6^- counterions. All the experimental isotope patterns were in good agreement with the theoretical ones (Fig. S8 and S10, ESI†). Given the aforementioned results, we inferred that **T** was self-assembled into a triangular-prismatic [M_6**T**$_3$] architecture (Scheme 1) with D_{3h} point-group symmetry. The C_3 axis lies perpendicularly on the center of triangular faces formed by the $\langle M^{II}\rangle$ edges, which resulted in the same chemical environment for all the tpy moieties.

Attempts to grow single crystals suitable for X-ray analysis by vapor diffusion were unsuccessful. Thus, electrospray ionization mass spectrometry (ESI-MS) coupled with traveling wave ion-mobility (TWIM) analysis[10] was utilized to further investigate the formation of [M_6**T**$_3$] prisms. Both Cd^{II} and Zn^{II} complexes gave the expected step patterns (Fig. 2b and Fig. S11, ESI†),[11] suggesting that all the signals purely resulted from the [M_6**T**$_3$] prisms in the absence of other isomers. The experimental collision cross-sections (CCSs) obtained from the corresponding charge states (Table S1, ESI†) are consistent with the theoretical average CCSs, again supporting the presence of the proposed architectures. Furthermore, the individual cages of [Cd_6**T**$_3$] with an average diameter of 2.1 ± 0.3 nm were visualized by TEM (Fig. 2c).

Since the prismatic cages possess three DB24C8 moieties, it is expected that [Cd_6**T**$_3$] and [Zn_6**T**$_3$] may accommodate a three-armed guest molecule through hydrogen bonding, ion–dipole, and π–π interactions[12] to afford metallo-supramolecular pseudo-suit[3]anes. The computational result (Fig. S23, ESI†) showed that a C6 alkyl linker is suitable for the three arms to fully thread into the crown ether rings of [Cd_6**T**$_3$]. Accordingly, the tris(dibenzylammonium)·3PF_6 salt (**TriG**) with a 1,3,5-substituted benzene core was synthesized (Scheme S2, ESI†). Firstly, three C6 linkers were attached to the central benzene ring *via* etherification of phloroglucinol with TBDMS-protected 6-bromohexanol, and the key intermediate, a trisaldehyde, was prepared by the subsequent deprotection of silyl groups, tosylation, and substitution with 4-hydroxybenzaldehyde. Eventually, **TriG** was obtained by the imination of the trisaldehyde with benzylamine, reduction with $NaBH_4$, protonation, and counterion exchange. The structure of **TriG** was unequivocally established by the NMR (Fig. 3c and Fig. S20, S21, ESI†) and ESI-MS (Fig. S22, ESI†) experiments.

The host–guest complexation was carried out by adding an equimolar amount of **TriG** into a CD_3CN solution (0.8 mM) of [Cd_6**T**$_3$]. The time-dependent ^{1}H NMR experiments (Fig. S24, ESI†) indicated that the solution reached equilibrium after

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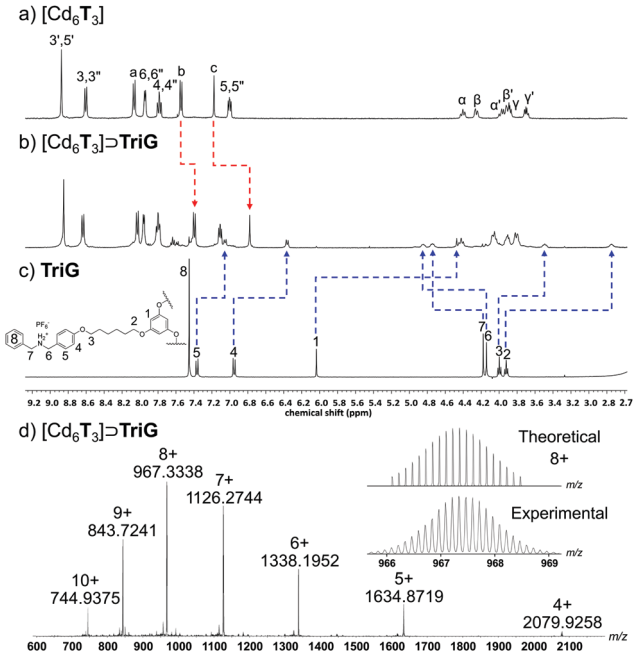


Fig. 3 ^{1}H NMR spectra of (a) [Cd_6**T**$_3$], (b) [Cd_6**T**$_3$]⊃**TriG**, and (c) **TriG** in CD_3CN and (d) ESI-MS spectrum of [Cd_6**T**$_3$]⊃**TriG**.

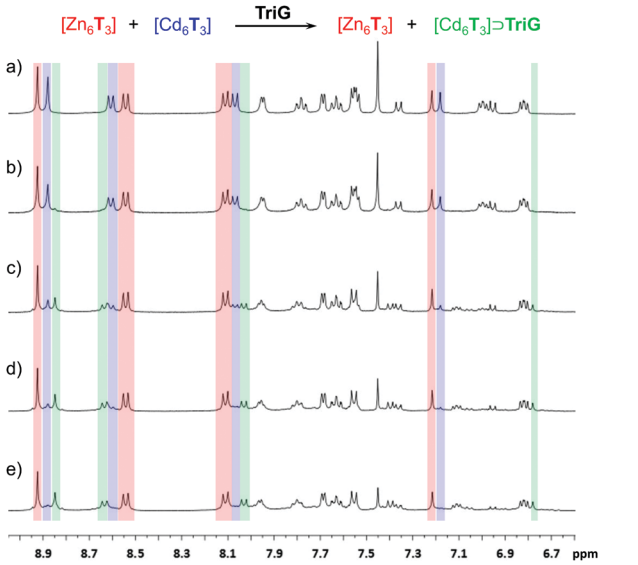


Fig. 4 Time-dependent ^{1}H NMR spectra (from a to e: 0.3, 2.7, 15.3, 22.0, and 40.8 h) of the inclusion process of **TriG** in the presence of an equimolar amount of [Zn_6**T**$_3$] (red) and [Cd_6**T**$_3$] (blue). The characteristic signals of [Cd_6**T**$_3$]⊃**TriG** are labeled in green.

2 days at 25 °C. In comparison with uncomplexed [Cd_6**T**$_3$] and **TriG**, the ^{1}H NMR spectrum (Fig. 3b) exhibited a series of signals assigned to the inclusion complex [Cd_6**T**$_3$]⊃**TriG**, and the host–guest stoichiometry was determined to be 1 : 1 by ^{1}H NMR peak integration and ESI-MS spectrometry (Fig. 3d and Fig. S28, ESI†). The ^{1}H NMR signals for the benzylic protons (H^6 and H^7) of **TriG** were shifted downfield (Fig. 3b), suggesting the formation of [+N–C–H···O] hydrogen bonds[12] in the threaded complex composed of the DB24C8 and dibenzylammonium motifs. The distinct upfield shifts for $H^{b,c}$ of [Cd_6**T**$_3$] and $H^{4,5}$ of **TriG** can be rationalized by the occurrence of π–π stacking between the pincer-like DB24C8 unit and the benzene ring of **TriG**. The hexyl protons and the central aromatic H^1 of **TriG** were shielded by the prismatic cage. In addition, the DOSY spectrum (Fig. S25, ESI†) showed that all the corresponding peaks of [Cd_6**T**$_3$]⊃**TriG** have the same diffusion coefficient that is smaller than that of free **TriG**. The above observations strongly supported that **TriG** located inside the cage, and the arms with dibenzylammonium ions threaded through the crown ethers inside out. These results were further confirmed by the through-space correlations between [Cd_6**T**$_3$] and **TriG** found in the ROESY NMR experiment (Fig. S27, ESI†). The association constant (K_a) of [Cd_6**T**$_3$]⊃**TriG**, a slow-exchange system, was estimated by using a single-point method[13] based on the ^{1}H NMR peak integration of the complexed and uncomplexed species (Fig. S29, ESI†), and was found to be 2.39 ± 0.37 × 10^4 M^{-1} in CD_3CN at 25 °C, which is about 60 times higher than that of the 1 : 1 complex of DB24C8 and dibenzylammonium·PF_6.[12] It is noteworthy that [Cd_6**T**$_3$]⊃**TriG** could be decomplexed by treatment with DBU to regenerate the parent metalloprism (Fig. S30, ESI†).

The complexation of **TriG** with [Zn_6**T**$_3$] was examined in the same manner. However, a much slower inclusion process was observed by ^{1}H NMR (Fig. S31, ESI†). The solution took 21 days to reach 32% conversion of [Zn_6**T**$_3$]⊃**TriG** in CD_3CN at 25 °C, presumably due to relatively kinetically inert ⟨Zn^{II}⟩ connectivity as compared to ⟨Cd^{II}⟩.[9,14] The low reversibility was also reflected in the self-assembly of [Zn_6**T**$_3$], which required a longer time and a higher temperature to afford the well-defined structure. Hence, in order to drive the equilibrium toward the Zn^{II} pseudo-suit[3]ane side, an MeCN solution of [Zn_6**T**$_3$] and **TriG** in a 1 : 3 molar ratio was refluxed for 2 days, and then the excess **TriG** was removed by MeOH to give [Zn_6**T**$_3$]⊃**TriG** in 89% yield. The structure was unambiguously established by NMR and ESI-MS (Fig. S32 and S33, ESI†).

Building on the metal ion-dependent kinetic variation, the host–guest chemistry in the presence of two different metallosuits was investigated. The inclusion process was monitored by ^{1}H NMR and ESI-MS (Fig. 4 and Fig. S35, ESI†). Interestingly, it was found that **TriG** was mainly encapsulated within [Cd_6**T**$_3$] at 25 °C on the second day after the addition of an equimolar mixture of Cd^{II} and Zn^{II} prisms, again implying that the host–guest inclusion process could be selectively controlled by the dynamicity of the metalloprisms. Moreover, the transmetalation between [Zn_6**T**$_3$] and [Cd_6**T**$_3$] or [Cd_6**T**$_3$]⊃**TriG** was markedly slowed down (Fig. S37b and c, ESI†). In sharp contrast, in the absence of **TriG**, the metalloprisms were rapidly scrambled within 5 h (Fig. S34 and S37a, ESI†). To gain more insight into the assembly mechanism, the stability of [Cd_6**T**$_3$] and [Cd_6**T**$_3$]⊃**TriG** was evaluated by tandem mass spectrometry.[15] The 8+ ions for each analyte were selected as precursors and subjected to collision-induced dissociation (CID) at varying ion trap voltages (Fig. S38, ESI†). The result revealed that a higher voltage was needed to fully dissociate [Cd_6**T**$_3$]⊃**TriG** into fragments in comparison to [Cd_6**T**$_3$], suggesting that the pseudo-suit[3]ane was further stabilized by the encapsulated **TriG** so that the enhanced

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stability not only drove the reaction toward $[Cd_6\mathbf{T}_3]\supset$**TriG**, but also decelerated transmetalation of the Cd^{II} pseudo-suit[3]ane.

In conclusion, two hexanuclear metalloprisms have been successfully prepared in quantitative yields by self-assembly of crown ether-based tetrakis(terpyridine)s with Cd^{II} and Zn^{II} ions, respectively. The prismatic hosts were able to accommodate the predesigned guest **TriG** to generate the pseudo-suit[3]anes, and the host–guest inclusion process was significantly influenced by the dynamic nature of metal–ligand coordinative interactions, which gave rise to selective formation of $[Cd_6\mathbf{T}_3]\supset$**TriG** in the presence of both metalloprisms. This metal ion-modulated encapsulation event provides a new way for exploiting more sophisticated self-assembly behavior *via* kinetic control in supramolecular chemistry.

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Notes and references

1 (*a*) E. Mandelkow, E.-M. Mandelkow, H. Hotani, B. Hess and S. C. Muller, *Science*, 1989, **246**, 1291; (*b*) E. Fuchs and D. W. Cleveland, *Science*, 1998, **279**, 514; (*c*) L. M. Utschig and M. C. Thurnauer, *Acc. Chem. Res.*, 2004, **37**, 439; (*d*) P. L. Kastritis and A. M. J. J. Bonvin, *J. R. Soc., Interface*, 2013, **10**, 20120835.

2 (*a*) J.-P. Sauvage and P. Gaspard, *From Non-Covalent Assemblies to Molecular Machines*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, p. 467; (*b*) J. G. Hardy, *Chem. Soc. Rev.*, 2013, **42**, 7881; (*c*) C. J. Brown, F. D. Toste, R. G. Bergman and K. N. Raymond, *Chem. Rev.*, 2015, **115**, 3012.

3 (*a*) J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2015, **54**, 3276; (*b*) E. R. Kay and D. A. Leigh, *Angew. Chem., Int. Ed.*, 2015, **54**, 10080; (*c*) A. J. McConnell, C. S. Wood, P. P. Neelakandan and J. R. Nitschke, *Chem. Rev.*, 2015, **115**, 7729; (*d*) M. Barboiu, A.-M. Stadler and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2016, **55**, 4130.

4 (*a*) F. Aricó, J. D. Badjic, S. J. Cantrill, A. H. Flood, K. C.-F. Leung, Y. Liu and J. F. Stoddart, in *Templates in Chemistry II*, ed. C. A. Schalley, F. Vögtle and K. H. Dötz, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, p. 203; (*b*) R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434.

5 (*a*) A. R. Williams, B. H. Northrop, T. Chang, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 2006, **45**, 6665; (*b*) B. H. Northrop, F. Aricó, N. Tangchiavang, J. D. Badjić and J. F. Stoddart, *Org. Lett.*, 2006, **8**, 3899.

6 (*a*) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (*b*) K. Harris, D. Fujita and M. Fujita, *Chem. Commun.*, 2013, **49**, 6703; (*c*) G. R. Newkome and C. N. Moorefield, *Chem. Soc. Rev.*, 2015, **44**, 3954; (*d*) T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001; (*e*) L. Chen, Q. Chen, M. Wu, F. Jiang and M. Hong, *Acc. Chem. Res.*, 2015, **48**, 201.

7 (*a*) H.-B. Yang, K. Ghosh, B. H. Northrop, Y.-R. Zheng, M. M. Lyndon, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2007, **129**, 14187; (*b*) S.-L. Li, T. Xiao, C. Lin and L. Wang, *Chem. Soc. Rev.*, 2012, **41**, 5950; (*c*) M. L. Saha, S. De, S. Pramanik and M. Schmittel, *Chem. Soc. Rev.*, 2013, **42**, 6860; (*d*) S. Li, J. Huang, T. R. Cook, J. B. Pollock, H. Kim, K.-W. Chi and P. J. Stang, *J. Am. Chem. Soc.*, 2013, **135**, 2084; (*e*) S. Li, J. Huang, F. Zhou, T. R. Cook, X. Yan, Y. Ye, B. Zhu, B. Zheng and P. J. Stang, *J. Am. Chem. Soc.*, 2014, **136**, 5908; (*f*) P. Wei, X. Yan and F. Huang, *Chem. Soc. Rev.*, 2015, **44**, 815; (*g*) T. Wu, Y. Guo, J. Yuan, Z. Jiang, D. Liu and P. Wang, *RSC Adv.*, 2015, **5**, 1754; (*h*) I. Linder, S. Leisering, R. Puttreddy, N. Rades, K. Rissanen and C. A. Schalley, *Chem. – Eur. J.*, 2015, **21**, 13035.

8 (*a*) C. Wang, X.-Q. Hao, M. Wang, C. Guo, B. Xu, E. N. Tan, Y.-Y. Zhang, Y. Yu, Z.-Y. Li, H.-B. Yang, M.-P. Song and X. Li, *Chem. Sci.*, 2014, **5**, 1221; (*b*) M. Wang, C. Wang, X.-Q. Hao, X. Li, T. J. Vaughn, Y.-Y. Zhang, Y. Yu, Z.-Y. Li, M.-P. Song, H.-B. Yang and X. Li, *J. Am. Chem. Soc.*, 2014, **136**, 10499; (*c*) J. M. Ludlow III, T. Xie, Z. Guo, K. Guo, M. J. Saunders, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Chem. Commun.*, 2015, **51**, 3820; (*d*) T.-Z. Xie, K. Guo, Z. Guo, W.-Y. Gao, L. Wojtas, G.-H. Ning, M. Huang, X. Lu, J.-Y. Li, S.-Y. Liao, Y.-S. Chen, C. N. Moorefield, M. J. Saunders, S. Z. D. Cheng, C. Wesdemiotis and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2015, **54**, 9224; (*e*) T.-Z. Xie, K. J. Endres, Z. Guo, J. M. Ludlow, C. N. Moorefield, M. J. Saunders, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2016, **138**, 12344.

9 U. S. Schubert, A. Winter and G. R. Newkome, *Terpyridine-Based Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011.

10 (*a*) Y.-T. Chan, X. Li, M. Soler, J.-L. Wang, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2009, **131**, 16395; (*b*) E. R. Brocker, S. E. Anderson, B. H. Northrop, P. J. Stang and M. T. Bowers, *J. Am. Chem. Soc.*, 2010, **132**, 13486; (*c*) 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; (*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*) F. Lanucara, S. W. Holman, C. J. Gray and C. E. Eyers, *Nat. Chem.*, 2014, **6**, 281.

11 X. Li, Y.-T. Chan, G. R. Newkome and C. Wesdemiotis, *Anal. Chem.*, 2011, **83**, 1284.

12 P. R. Ashton, P. J. Campbell, P. T. Glink, D. Philp, N. Spencer, J. F. Stoddart, E. J. T. Chrystal, S. Menzer, D. J. Williams and P. A. Tasker, *Angew. Chem., Int. Ed.*, 1995, **34**, 1865.

13 (*a*) C. Li, Q. Xu, J. Li, Y. Feina and X. Jia, *Org. Biomol. Chem.*, 2010, **8**, 1568; (*b*) J.-M. Zhao, Q.-S. Zong, T. Han, J.-F. Xiang and C.-F. Chen, *J. Org. Chem.*, 2008, **73**, 6800; (*c*) L. Li and G. J. Clarkson, *Org. Lett.*, 2007, **9**, 497; (*d*) D. Castillo, P. Astudillo, J. Mares, F. J. Gonzalez, A. Vela and J. Tiburcio, *Org. Biomol. Chem.*, 2007, **5**, 2252; (*e*) A. B. Braunschweig, C. M. Ronconi, J.-Y. Han, F. Aricó, S. J. Cantrill, J. F. Stoddart, S. I. Khan, A. J. P. White and D. J. Williams, *Eur. J. Org. Chem.*, 2006, 1857; (*f*) S. J. Loeb, J. Tiburcio and S. J. Vella, *Org. Lett.*, 2005, **7**, 4923; (*g*) S. J. Loeb and J. A. Wisner, *Angew. Chem., Int. Ed.*, 1998, **37**, 2838.

14 (*a*) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle and R. G. Wilkins, *Inorg. Chem.*, 1966, **5**, 622; (*b*) C. Bazzicalupi, A. Bencini, A. Bianchi, A. Danesi, E. Faggi, C. Giorgi, S. Santarelli and B. Valtancoli, *Coord. Chem. Rev.*, 2008, **252**, 1052.

15 (*a*) L. Sleno and D. A. Volmer, *J. Mass Spectrom.*, 2004, **39**, 1091; (*b*) Y.-P. Liang, Y.-J. He, Y.-H. Lee and Y.-T. Chan, *Dalton Trans.*, 2015, **44**, 5139.