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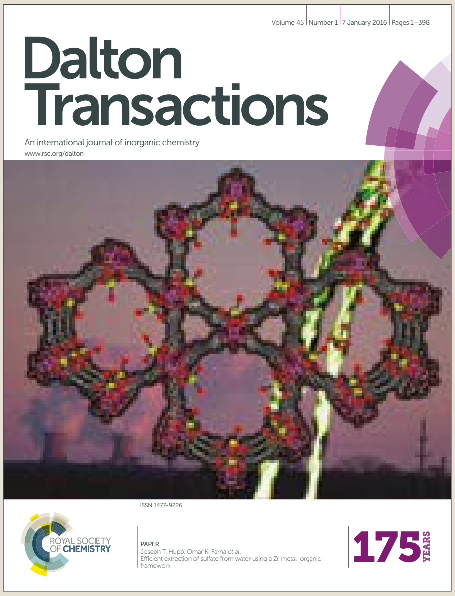

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Terpyridine-based Metallo-organic Cage and Supramolecular Gelation by Coordination-driven Self-assembly and Host–guest Interaction

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Host-guest complexation based on terpyridine (tpy) three-dimensional (3D) metallo-cages received less attention due to the complicated structure and solubility issue. Herein, a three-armed metallo-organic ligand (**L**) was synthesized *via* three 120°-bent bis-tpy groups into rigid *tetrakis*-tpy core, which possesses one benzo-21-crown-7 (B21C7) for further host-guest interaction. The metallo-organic cages [**M_3L_2**] with molecular weight up to 13,000 Da and a giant cavity was prepared in near-quantitative yield by self-assembly of **L** with metal ions, such as Zn^{2+} and Fe^{2+}. The 3D metallo-supramolecules were characterized and supported by NMR, DOSY, ESI-MS and TEM. Hosts [**M_3L_2**] were threaded through a difunctional alkylammonium salt by host–guest interactions to polymerize, and subsequently generate the novel metallo-gels between [**Zn_3L_2**] and bis-ammonium salt (**N^2**).

Introduction

Supramolecular self-assembly is a key process in life systems to create abundant well-defined abiological architectures with special functionalities, such as DNA double helical structure[1] and viral capsid[2-4]. In the journey of mimicking biological systems, a variety of non-covalent interactions has been exploited to construct the functionalized supramolecular self-assemblies, such as van der Waals, π–π stacking, hydrogen bonding, metal–ligand interactions, etc.[5-7] Among these interactions, coordination-driven terpyridinyl self-assembly of discrete supramolecular architectures with predesigned, well-defined sizes and shapes has drawn extensive attentions due to their highly directional and predictable feature. Up to date, a series of terpyridine supramolecules have been successfully prepared, from two-dimensional (2D) macrocycles,[4] spoked wheel[5] and fractals[6] to three dimensional (3D) cages[7] and polyhedrons.[8] However, the functionalization of this kind of supramolecular architectures was rare.[9]

To construct more elaborate and complex metallo-supra-architectures and to further realize the functionality, the step-wise assembly was frequently used as an alternative strategy, when one-pot self-assembly was unable to construct complex architectures under thermodynamic control.[10] More recently, using the step-wise strategy on stable tpy-Ru^{2+}-tpy metallo-organic ligand (MOL) to assemble complicated and yet elegant metallo-supramolecule has been demonstrated to create the 2D or 3D architectures with large molecular weights.[11] This strategy thoroughly avoids the self-sorting of polyterpyridinyl subcomponents and provides possibility for the self-assembly of desired multicomponent 2D or 3D supra-structures. Furthermore, the functional moieties anchored on terpyridinyl precursor could be conveniently introduced into supramolecule *via* stable tpy-Ru-tpy complexity.

Crown ether host/guest reciprocal interactions, which exhibited better selectivity, higher efficiency and peculiar reversibility, have been widely employed in the construction of supramolecular materials.[12] Therefore, taking advantage of the coordination-driven self-assembly and host-guest interactions between crown ether and ammonium substrates to construct a supramolecular system is feasible and meaningful.[13] Herein, using the step-wise strategy and *tetrakis*(4-(4-(4'-[2,2':6',2''] terpyridyl) phenyl) phenyl)methane as the rigid core, the metallo-organic ligand **L** with three uncomplexed terpyridinyl arms in nearly parallel juxtaposition were synthesized by sequentially incorporating one benzo-21-crown-7 (B21C7) functionalized terpyridine and three 120°-bent *bis*-terpyridine *via* the terpyridine-Ru^{2+}-terpyridine (<tpy-Ru^{2+}-tpy>)

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† Electronic Supplementary Information (ESI) available: Full experimental details, the ^1H NMR, ^{13}C NMR, COSY, ROESY, and UV spectra of the new compounds, ESI-MS spectra of related compounds. See DOI: 10.1039/x0xx00000x
‡ These authors contributed equally to this work.

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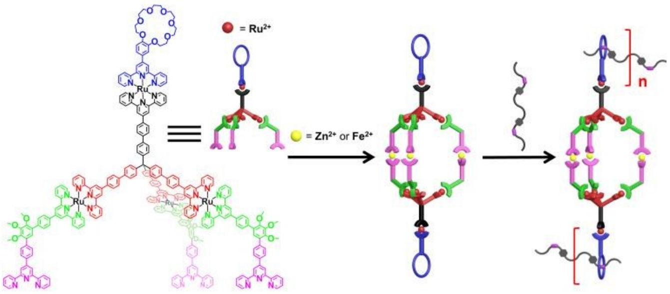


Scheme 1 Schematic illustration of preparing *di*metallo-organic supramolecular cages [$\mathbf{M_3L_2}$] (**M** =Zn^{2+} or Fe^{2+}) and host–guest interactions with symmetrical difunctional alkylammonium salt $\mathbf{N^2}$.

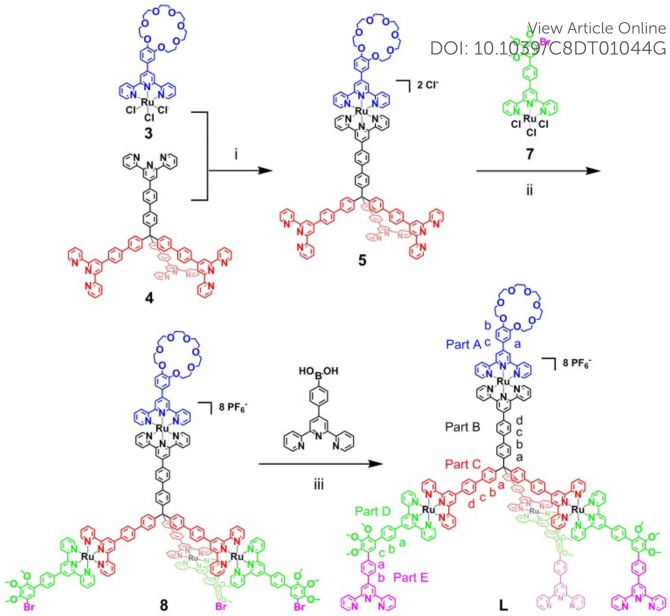
coordination linkages. Subsequently, two crown ethers contained terpyridinyl metallo-organic cages [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were readily prepared *via* self-assembly of ligand **L** with metal ion (Zn^{2+} or Fe^{2+}). The host-guest interaction between crown ether-cages (host) and alkyl-ammonium salt was confirmed, and the thermodynamically controlled metallo-gel was prepared *via* polymerization by using bis-ammonium salt $\mathbf{N^2}$ (scheme **1**).

Results and discussion

Tetrakisterpyridine compound **4** (scheme **2**) was prepared by Suzuki coupling from tetrakis(4-bromophenyl)methane according to previous report.[14] The trifurcated free-terpyridine **5** was obtained as a red solid by stirring Ru^{3+} monoadduct **3** with excess compound **4** in $CH_3OH/CHCl_3$ (v/v 2:1) in the presence of N-ethylmorpholine for 24 h and purified by the flash column chromatography (Al_2O_3, $CHCl_3$/MeOH). Similarly, the key precursor Br-substituted complex **8** was readily synthesized from **5** by treatment with 3.6 eq. Ru^{3+} monoadduct **7**. ^{1}H NMR of complex **8** displayed three sharp singlets of methoxy group at 4.95, 3.87 and 3.72ppm with a 1:1:1 integration ratio (Figs. S16-S18, ESI†), agreeing well with the expected structure. The key metallo-organic ligand **L** was prepared *via* a final Suzuki coupling with **8** and {4'-(4-boronatophenyl)[2,2':6',2'']} terpyridine and further purified by flash column chromatography (Al_2O_3) eluting with CH_2Cl_2/CH_3OH. The methoxyl groups at the corner of three 120°-bent bis-terpyridine have been introduced for significantly enhancing the solubility.

^{1}H NMR of ligand **L** was discernible compared to its precursor **8**. A new singlet for tpy$H^{3',5'}$ signals at 8.77ppm showed an up-shift compared with coordinated tpy$H^{3',5'}$ peaks in <tpy-Ru^{II}-tpy>, suggesting three free terpyridine moieties were successfully incorporated. Moreover, the high-resolution ESI-MS confirmed the structure **L** as *m/z*: 1065.09 $[M-5PF_6^-]^{5+}$ (calcd. *m/z* = 1065.06) and 863.42 $[M-6PF_6^-]^{6+}$ (calcd. *m/z* = 863.39). The measured isotopic patterns of **L** were consistent with the calculated peaks (Fig. S3, ESI†).

Metallo-organic cages [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were prepared (scheme **3**) by mixing **L** and $Zn(NO_3)_2$ (or $FeCl_2$) in a precise stoichiometric ratio of 2:3 in MeCN, followed by adding excess NH_4PF_6 solution to afford a red precipitate, which was washed with pure water and dried in vacuo. Although the cages [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] contained 11 metal ions and 22 tpy moieties, both complexes were soluble in MeCN due to the multiple methoxy and crown ether moieties. [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were determined by ^{1}H NMR, COSY, NOESY, DOSY, ESI-MS spectroscopies along with TEM. However, attempt to grow X-ray quality single crystals of [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] was unsuccessful possibly due to its relatively flexible structure.[8c]



Scheme 2 Synthesis of Ligands **L**: (i,ii) N-ethylmorpholine, $CHCl_3/CH_3OH$, refluxed; (iii) $Pd(PPh_3)_4$, K_2CO_3, CH_3CN, refluxed.

^{1}H NMR of complexes [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] (Figure **1**) showed comparatively distinct patterns for the expected peaks, but the notable attributes were complicated caused by the multiple complexation environment from different tpy moieties. The characteristic signals were observed for the tpy$H^{3',5'}$ protons (at 9.10 ppm for [$\mathbf{Zn_3L_2}$] and 9.27 ppm for [$\mathbf{Fe_3L_2}$]) from tpy part-E, which showed significantly downfield-shift compared with **L** at 8.77 ppm.

Also, the tpy$H^{6,6''}$protons moved significantly upfield owing to electron shielding effects after coordination. The broad ^{1}H NMR signals could be rationalized by the large cage-like complexes, which have slow tumbling motion on the NMR time scale.[15] Although there were multiple sets of protons of tpy and phenyl units for the results of substantial overlap of the multiple tpy moieties, the corresponding peaks of five different tpy units with the expected integration ratio could been successfully assigned based on the analysis of 2D COSY and 2D ROESY NMR spectra.

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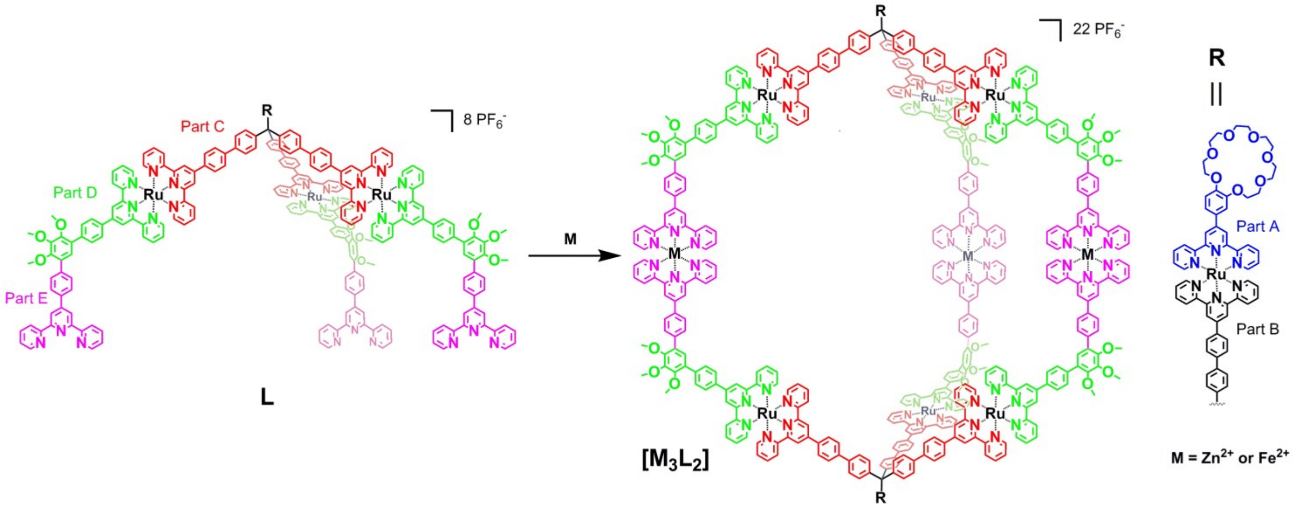

Scheme 3 Metallo-organic ligand **L** and self-assembly of bimetallo-organic cages [$\mathbf{M_3L_2}$] (**M** =Zn^{2+} or Fe^{2+}).

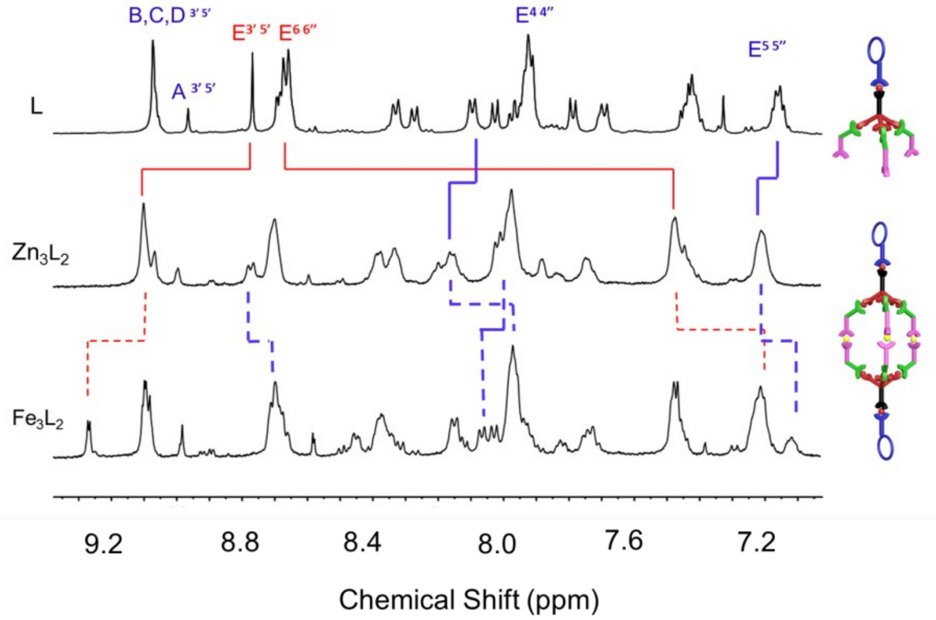

Fig. 1 Partial ^{1}H NMR spectra (500 MHz) of metallo-organic ligand **L**, supramolecular cage [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] in CD_3CN.

Diffusion-ordered NMR spectroscopies (DOSY) of ligand **L**(Fig. S22, ESI†), complexes [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were shown Figure **2** for [$\mathbf{Fe_3L_2}$] and Fig.S26 for [$\mathbf{Zn_3L_2}$]. In DOSY, the observation of a distinct band of [$\mathbf{Fe_3L_2}$] showed a narrow band at log D= -9.85, indicating the formation of a single discrete product. Similarly, the log D = -9.82 of [$\mathbf{Zn_3L_2}$] was approximately close to that of [$\mathbf{Fe_3L_2}$]. The near diffusion coefficient of 1.51 × 10^{-10} m^2 s^{-1} for [$\mathbf{Fe_3L_2}$] and 1.41 × 10^{-10} m^2 s^{-1} for [$\mathbf{Zn_3L_2}$] demonstrated that both cage-like structures possessed similar size and connectivity. Further, the dynamic diameter was calculated to be 7.8 nm for [$\mathbf{Fe_3L_2}$] and 8.4 nm for [$\mathbf{Zn_3L_2}$] which were approximately equal to twice of 5.1 nm for **L**, demonstrating the forming of cage-like structure.

Metallo-cages [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were further characterized by ESI-MS to endorse the proposed structures with molecular weights of 13166.8 Da and 13137.8 Da,

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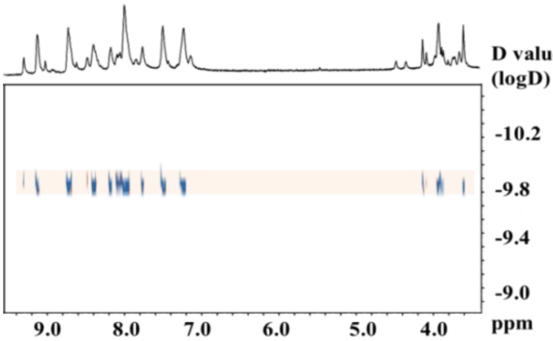

Fig. 2 DOSY spectrum (500 MHz) of supramolecular cage [$\mathbf{Fe_3L_2}$] in CD_3CN.

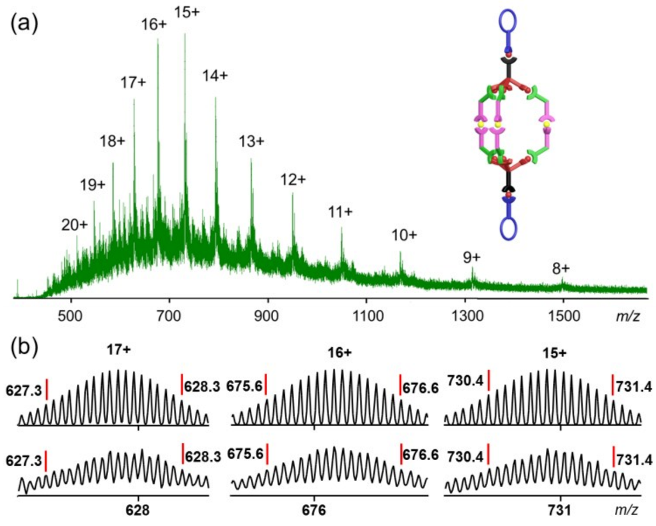

Fig. 3 ESI-MS spectrum of cage [$\mathbf{Fe_3L_2}$].

respectively. In ESI-MS, the charge states of integrated assemblies were exhibited. A series of dominant peaks of [$\mathbf{Fe_3L_2}$] were detected corresponding to charge states of 8^+ to 20^+ generated by the loss numbers of PF_6^- anions and corresponding experimental isotope patterns were in well agreement with the calculated patterns (Fig. 3 and Fig. S7, ESI †). Similarly, [$\mathbf{Zn_3L_2}$] was observed a series of peaks from 7^+ to 16^+ (Fig. S4, ESI†) and were isotopically resolved in excellent agreement with their calculated theoretical distributions (Fig. S5, ESI†). There existed the bumpy ground line in the mass spectrum may due to the encapsulation of solvent or salt molecules inside the cage.[8(c),16]

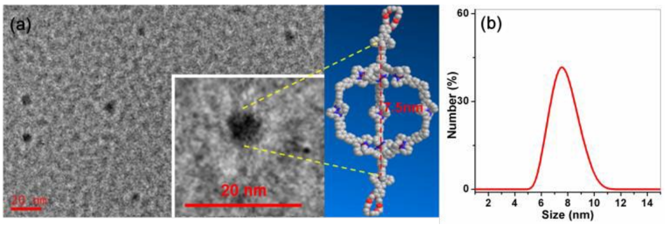

Fig. 4 (a)TEM image of supramolecular cage [$\mathbf{Fe_3L_2}$] and representative energy-minimized structure from molecular modeling. (b) the dynamic light scattering (DLS) graph of cage [$\mathbf{Zn_3L_2}$].

The size and shape of [$\mathbf{Fe_3L_2}$] were imaged by transmission electron microscopy (TEM) (Fig. **4**). The TEM images manifested highly dispersed [$\mathbf{Fe_3L_2}$] with an approximate length of 7.5 nm and width of 4.2nm respectively, in close agreement with values obtained from molecular modelling (Fig. **4**,right). And corresponding TEM images of [$\mathbf{Zn_3L_2}$] was shown in Fig. S31. Further, the average diameter of cages [$\mathbf{Zn_3L_2}$] and [$\mathbf{Fe_3L_2}$] were determined to be 7.5 nm by the DLS experiment, which supporting the forming of cages (Fig. **4**(b) and Fig. S32).

To evaluate the feasibility of complicated host/guest threaded structures, [$\mathbf{Zn_3L}$] and [$\mathbf{Fe_3L_2}$] were dissolved in $CH_3CN/CHCl_3$ (1:2) and then ammonium salt as guest was added with same solvent proportion. Partial proton ^{1}H NMR experiments furnished insights into the complexations of [$\mathbf{Zn_3L_2}$] or [$\mathbf{Fe_3L_2}$] with ammonium salt guests ($\mathbf{N^1}$), respectively (shown in Fig. **5**(b), Fig. S36, ESI†). Comparisons of ^{1}H NMR spectrum of [$\mathbf{Zn_3L_2}$], ammonium salt and their mixture revealed the apparent chemical shift changes. As shown in Fig. **5**(b), the partial crown ether ^{1}H NMR spectrum of the mixtures was complicated and divided into five sets which were corresponding to the complex species. Due to the 3D hosts possessing the molecular weights of over 13 kDa, crown ether protons all shifted slightly. Downfield chemical shift changes were observed for ethylenoxy protons of $H^{a,b}$, $H^{c,d}$, $H^{e,f}$, H^i, while $H^{g,h}$ shifted upfield after complexation, which was in accordance with the well-known B21C7/alkylammonium complexation motif.[17]

The supramolecular metallo-gel was prepared *via* polymerization of [$\mathbf{Zn_3L_2}$] and bis-ammonium salt ($\mathbf{N^2}$) (Fig. **6**a). [$\mathbf{Zn_3L_2}$] in mixed CH_3CN/H_2O solution at ambient temperature. Supramolecular network and gelation were observed with the gradual increase of viscosity in results of linkage between B21C7 and ammonium salt moieties. When [$\mathbf{Zn_3L_2}$] (host) interacted with $\mathbf{N^2}$ (guest), there were some structural forms in this gel, such as intertwined dimers, oligomers and polymers.[18] According to metallo-organic gel, herein, we could deduce that the polymers played a dominant role. As shown in Figs. **6**(b,c), S40 and S41, the fabrication of gel was examined by TEM, scanning electron microscopy (SEM) and atomic force microscope (AFM). Although the SEM and AFM images did not indicate the obvious fibrous morphology, the TEM image exhibited an entangled extended and interconnected fibrous network indicative of the polymeric network formation.

Conclusions

In summary, we have demonstrated a highly efficient approach of constructing host-guest complexations of tpy-based three-dimensional (3D) dinuclear metallo-organic cages. By careful design of 120°-bent tpy groups into rigid core, thenovel bipyramidal structures functionalized with two crown-ether groups were successfully synthesized. Multiple NMR (^{1}H NMR, 2D COSY, NOESY and DOSY NMR) analysis supported the formation of discrete resultant products. ESI-MS, TEM and DLS provided the further evidences of precise molecular structures and exact molecular weights, molecular

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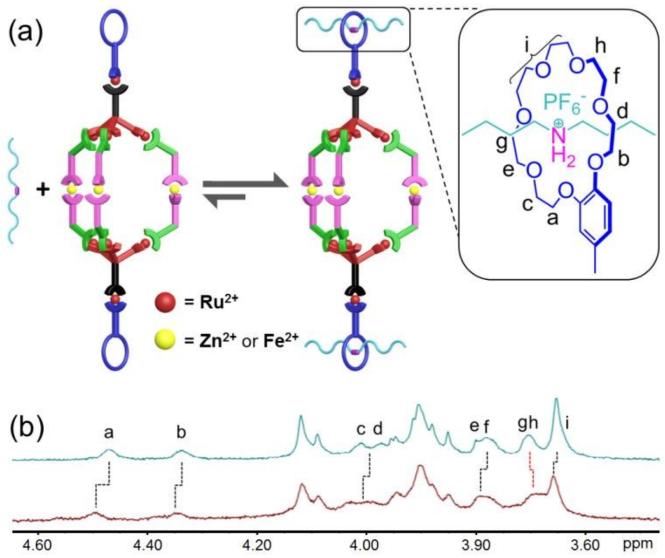

Fig. 5 (a) Schematic illustration of host–guest Interactions of crown ether (B21C7)-functionalized metallo-organic cages [**M_3L_2**] with secondary ammonium salt and (b) Partial ^{1}H NMR spectra (500 MHz, $CD_3CN/CDCl_3$, 298 K) of cage [**Fe_3L_2**] (top) and after adding **N^2** (bottom).

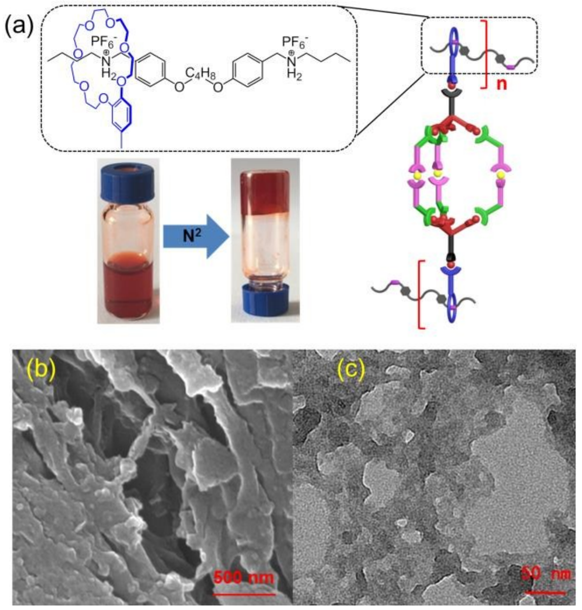

Fig. 6 (a) Illustration and photograph of gel formation; (b) SEM and (c) TEM images of gels formed with [**Zn_3L_2**] with bis-ammonium salt (**N^2**).

shapes and sizes. Moreover, the gelation of 3D cages and ammonium salt was investigated *via* host-guest interactions between B21C7 and **N^2**. This work will attract more attention on potential supramolecular polymer constructed by 3D metallo-organic cages and eventually will accomplish functional diversity. More importantly, such novel interaction among the functionalized infrastructure will push forward the development of terpyridinyl supramolecular chemistry.

Acknowledgements

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Notes and references

1 W. R. Wikoff, L. Liljas, R. L. Duda, H. Tsuruta, R. W. Hendrix and J. E. Johnson, *Science*, 2000, **289**, 2129.

2 (a) C. Abad-Zapatero, S. S. Abdel-Meguid, J. E. Johnson, A. G. W. Leslie, I. Rayment, M. G. Rossmann, D. Suck and T. Tsukihara, *Nature*, 1980, **286**, 33; (b)M. G. Rossmann, E. Arnold, J. W. Erickson, E. A. Frankenberger, J. P. Griffith, H.-J. Hecht, J. E. Johnson, G. Kamer, M. Luo, A. G. Mosser, R. R. Rueckert, B. Sherry and G. Vriend, *Nature*, 1985, **317**, 145; (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.

3 (a) J.-M. Lehn, *Angew. Chem., Int. Ed*., 1988, **27**, 89; (b) D. J. Cram, Angew. Chem., Int. Ed., 1988, **27**, 1009; (c) C. J. Pedersen, Angew. Chem., Int. Ed., 1988, **27**, 1021.

4 (a) G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush, P. S. Russo, *Angew. Chem., Int. Ed.*, 1999, **38**, 3717–3721; (b) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645–5647; (c) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem., Int. Ed.*, 1996, **35**, 1838–1840; (d) G.-H. Ning, T.-Z. Xie, Y.-J. Pan, Y.-Z. Li and S.-Y. Yu, *Dalton Trans.*, 2010, **39**, 3203–3211; (e) X. Yu, X. Li, Y. Cao, A. Schultz, J.-L. Wang, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2013, **52**, 7728–7731; (f) Y. M. Li, Z. Jiang, J. Yuan, T. Wu, C. N. Moorefield, G. R. Newkome, and P. S. Wang, *Chem. Commun.*, 2015, **51**, 5766–5769; (g) Y. M. Li, Z. L Jiang, M. Wang, J. Yuan, D. Liu, X. Y. Yang, M. Z Chen, J Yan, X. P. Li and P. S. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 10041–10046; (h) D. Liu, X. Yang, Y. Li and P. S. Wang, *Chem. Commun.*, 2016, **52**, 2513-2516.

5 J.-L. Wang, X. Li, X. Lu, I. F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng, G. R. Newkome, *J. Am. Chem. Soc.*, 2011, **133**, 11450–11453;

6 (a) G. R. Newkome, P. Wang, C. N. Moorefield, T. J. Cho, P. P. Mohapatra, S. Li, S. H. Hwang, O. Lukoyanova, L. Echegoyen, J. A. Palagallo, V. Iancu and S. W. Hla, *Science*, 2006, **312**, 1782. (b) R. Sarkar, K. Guo, C. N. Moorefield, M. J. Saunders, C. Wesdemiotis and G. R. Newkome, *Angew. Chem., Int. Ed.*, 2014, **53**, 12182–12185.

7 (a) M. Wang, C. Wang, X.-Q Hao, X. H. Li, T. J. Vaughn, Y.-Y. Zhang, Y. H. Yu, Z.-Y. Li, M.-P. Song, H.-B. Yang and X. P. Li, *J. Am. Chem. Soc.*, 2014, **136**, 10499–10507; (b) T.-Z. Xie, S.-Y. Liao, K. Guo, X. Lu, X. Dong, M. Huang, C. N. Moorefield, S. Z. D. Cheng, X. Liu, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2014, **136**, 8165–8168; (c) 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**, 12344-12347.

8 (a) T.-Z. Xie, K. Guo, Z. Guo, 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**, 9224–9229; (b) J. M. Ludlow III, T. Xie, Z.-H. Guo, K. Guo, M. J. Saunders, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Chem. Commun.*, 2015, **51**, 3820; (c) C. Wang, X.-Q Hao, M. Wang, C.-L Guo, B.-Q Xu, Eric N. Tan, Y.-Y Zhang, Y.-H Yu, Z.-Y Li, H.-B Yang, M.-P Song,

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X. P. Li, *Chem. Sci.*, 2014, **5**,1221-1226; (d) X. Lu, X. Li, K. Guo, T.-Z. Xie, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2014, **136**, 18149–18155; (e) X. Lu, X. Li, K. Guo, M. Huang, J.-L. Wang, T.-Z. Xie, C. N. Moorefield, S. Z. D. Cheng, C. Wesdemiotis and G. R. Newkome, *Chem. Eur. J.*, 2014, **20**, 13094–13098.

9 (a) L. Li, Y. Cong, L. He, Y. Wang, J. Wang, F.-M. Zhang, W. Bu, *Polym. Chem.*, 2016, **7**, 6288-6292; (b) J. Zhan, Q. Li, Q. Hu, Q. Wu, C. Li, H. Qiu, M. Zhang, S. Yin, *Chem. Commun.*, 2014, **50**, 722-724.

10 (a) G. R. Newkome, P. Wang, C. N. Moorefield, T. J. Cho, P. P. Mohapatra, S. Li, S.-H. Hwang, O. Lukoyanova, L. Echegoyen, J. A. Palagallo, *Science,* 2006, **312**, 1782; (b) H. Sepehrpour, M. L. Saha, P. J. Stang, *J. Am. Chem. Soc.,* 2017, **139**, 2553; (c) K. Li, L.-Y. Zhang, C. Yan, S.-C. Wei, M. Pan, L. Zhang, C.-Y. Su, *J. Am. Chem. Soc.,* 2014, **136**, 4456; (d) W. J. Ramsay, F. J. Rizzuto, T. K. Ronson, K. Caprice, J. R. Nitschke, *J. Am. Chem. Soc.*, 2016, **138**, 7264; (e) T. Nakamura, H. Kimura, T. Okuhara, M. Yamamura and T. Nabeshima, *J. Am. Chem. Soc.*, 2016, **138**, 794–797.

11 (a) D. Liu, Z. Jiang, M. Wang, X. Yang, H. Liu, M. Chen, C. N. Moorefield, G. R. Newkome, X. Li and P. Wang, *Chem. Commun.*, 2016, **52**, 9773-9776. (b) S. Chakraborty, W. Hong, K. J. Endres, T.-Z. Xie, L. Wojtas, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2017, **139**, 3012–3020. (c) Z. Zhang, H. Wang, X. Wang, Y. Li, B. Song, O. Bolarinw, R. A. Reese, T. Zhang, X.-Q. Wang, J. Cai, B. Xu, M. Wang, C. Liu, H.-B. Yang and X. Li, *J. Am. Chem. Soc.*,2017,**139**, 8174–8185 (d) Z. Jiang, Y. Li, M. Wang, B. Song, K. Wang, M. Sun, D. Liu, X. Li, J. Yuan, M. Chen, Y. Guo, X. Yang, T. Zhang, C. N. Moorefield, G. R. Newkome, B. Xu, X. Li and P. Wang, 2017, *Nat. Commun.* 2017, **8**, 15476; (e) Z. Jiang, Y. Li, M. Wang, D. Liu, J. Yuan, M. Chen, J. Wang, G. R. Newkome, W. Sun, X. Li and P. Wang. *Angew. Chem., Int. Ed.*, 2017, **56**, 11450.

12 (a) N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.,Int. Ed.*, 1998, **37**, 2361; (b) H. W. Gibson, Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522; (c) N. Huang and F. H. W. Gibson, *J. Am. Chem. Soc.*, 2004, **126**, 14738; (d) Z. Niu, F. Huang, H. W. Gibson, *J. Am. Chem. Soc.*, 2011, **133**, 2836; (e) A.-J. Avestro, M. E. Belowich and J. F. Stoddart, *Chem. Soc. Rev.*, 2012, **41**, 5881; (f) X. Ji, Y. Yao, J. Li, X. Yan and F. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 74.

13 (a) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem., Int. Ed.,* 2010, **49**, 1090; (b) 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.

14 T. Bauer, A. D. Schlüter, J. Sakamoto, *Synlett*., 2010, **6**, 877-880.

15 Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science*, 2010, **328**, 1144.

16 (a) B. Sun, M. Wang, Z. Lou, M. Huang, C. Xu, X. H. Li, L.-J. Chen, Y. Yu, G. L. Davis, B. Xu, H. B. Yang and X. P. Li, *J. Am. Chem. Soc.*,2015,**137**, 1556–1564. (b) B. Song, Z. Zhang, K. Wang, C.-H. Hsu, O. Bolarinwa, J. Wang, Y. Li, G.-Q. Yin, E. Rivera, H.-B. Yang, C. Liu, B. Xu and X. P. Li, *Angew. Chem., Int. Ed.,* 2017, **56**, 5258–5262.

17 (a) C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li and F. Huang, *Org. Lett.*, 2007, **9**, 5553-5557. (b) L. Chen, Y.-K. Tian, Y. Ding, Y.-J. Tian and F. Wang, *Macromolecules*, 2012, **45**, 8412-8419. (c) X. Yan, T. R. Cook, J. Bryant Pollock, P. Wei, Y. Zhang, Y. Yu, F. Huang and P. J. Stang, *J. Am. Chem. Soc.*, 2014, **136**, 4460-4463. (d) H. Li, X. Fan, W. Tian, H. Zhang, W. Zhang, Z. Yang, *Chem. Commun.*, 2014, **50**, 14666-14669. (e) X.-Y. Hu, T. Xiao, C. Lin, F. Huang and L. Wang. *Acc. Chem. Res.*, 2014, **47**, 2041-2051. (f) S. Dong, B. Zheng, F. Wang and F. Huang, *Acc. Chem. Res.*, 2014, **47**, 1982-1994.

18 (a) N. Yamaguchi and H. W. Gibson, Chem. Commun., 1999, 789–790. (b) H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522-3533.

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Terpyridine-based Metallo-Organic Cage and Its Supramolecular Gelation by Coordination-driven Self-Assembly and Host–Guest Interactions

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Dimetallo-cages engendered through a predesigned metallo-orangic ligand and Fe^{2+} (or Zn^{2+}). Cage connected with *Di*alkylammonium salt *via* host–guest interaction caused the thermodynamic polymer metallo-gel.