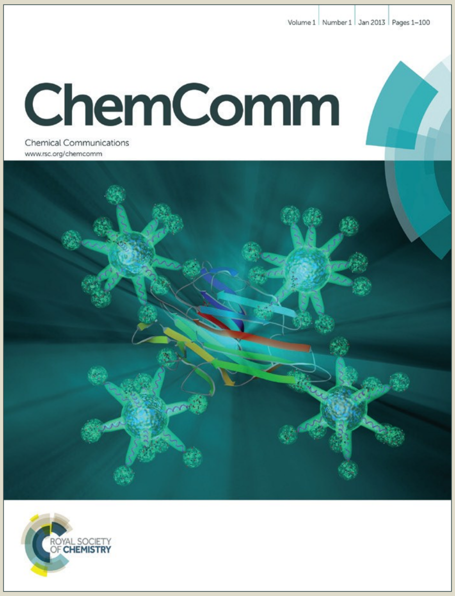
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Conformation driven *in situ* interlock: from discrete metallocycles to infinite polycatenane

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

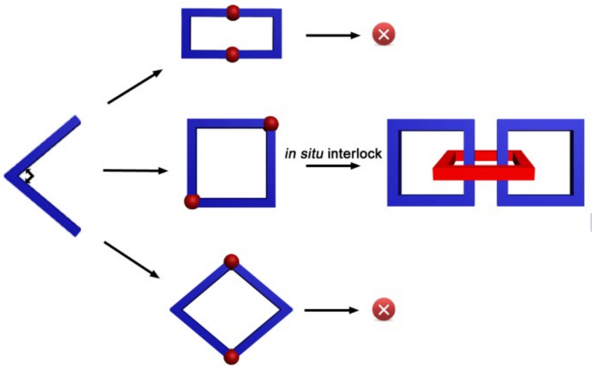
Hui Xue,[a,b] Feilong Jiang,[a] Qihui Chen,*[a] Daqiang Yuan,[a] Jiandong Pang,[a,b] Guangxun Lv,[a,b] Xiuyan Wan,[a,b] Linfeng Liang,[a,b] and Maochun Hong*[a]

c

A novel conformation driven self-assembly system, where four metallocycles with different conformations have been *in situ* self-assembled. Interestingly, only square metallocycles can further interlock into polycatenane. However, rectangular and rhombus metallocycles are failure to overcome such entropically unfavourable process, which constitutes an obstacle to the formation of polycatenane.

Supramolecular aggregates with well-defined shapes based on coordination have attracted considerable attention due to their aesthetically fascinating structures and possible applications particularly in the field of recognition, catalysis, and drug delivery.[1] Catenanes are a class of supramolecular assemblages consisting of interlocked macrocycles, ranging from simple single interlock to multiple interlock, which have drawn considerable attention not only for their interesting topological structures, but also for their astonishing applications such as in molecular machine;[2] and variety of directed templating techniques such as metal-template, donor–acceptor interactions have been developed to obtain such fascinating structures.[3] In fact, coordination-driven self-assembly without template also can lead to these higher order architectures via numerous association and dissociation steps. In 1994, Fujita group firstly synthesized a [2]catenane based on the *in situ* formed metal-organic rings.[4] Since then, many catenanes based on two dimensional metallocycles or three dimensional metallocages have been reported.[5] Infinite polycatenane[6] and polyrotaxane[7] with multiple interlocking knots seems hard to be assembled, so only several polycatenane chains based on discrete metalloassemblages have been reported, and the influences governing their self-assembly are still obscure. So how to construct such highly organized architectures from discrete metalloassemblages and insight into their self-assembly processes have therefore remained a challenge for chemists.

Herein, we develop a novel conformation driven self-assembly system, in which four metallocycles with different conformations have been *in situ* self-assembled, and only square metallocycles can *in situ* interlock into polycatenane while rectangular metallocycle and rhombus metallocycle cannot overcome such entropically unfavourable process.



Scheme 1 Conformation driven *in situ* interlock.

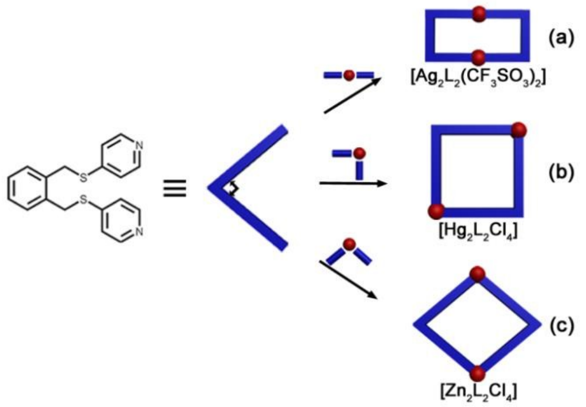
In order to construct different metallocycles, a flexible 'V' shape ligand L (L = 1,2-bis[(pyridin-4-ylthio)methyl]benzene), was used. The ligand contains rigid benzene ring, pyridyl group and soft methylene group, which is so flexible that it can adopt any angle from 0° to 180° to satisfy construction of metallocycles with different conformations based on suitable metal acceptor. For example, the Hg^{2+} is usually square four-coordinated, so that $HgCl_2$ will mostly react with L to form a square macrocycle $[Hg_2L_2Cl_4]$; the Ag^+ is usually linear two-coordinated, and a rectangular macrocycle $[Ag_2L_2(CF_3SO_3)_2]$ may be obtained from $AgCF_3SO_3$ with L; the Zn^{2+} is usually tetrahedral four-coordinated or octahedral six-coordinated, so that $ZnCl_2$ may react with L to form a rhombus macrocycle $[Zn_2L_2Cl_4]$. ESI-MS spectra demonstrate that each of three metallocycles can be quickly self-assembled from one

---

[a] State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
Fuzhou, Fujian, P. R. 350002, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China
*To whom correspondence should be addressed: Email: hmc@fjirsm.ac.cn; chenqh@fjirsm.ac.cn; Fax: +86-591-83794946; Tel:+86-591-83792460

† Electronic Supplementary Information (ESI) available: Additional details of experimental procedure, additional figures and ESI-MS spectra for compound **1-3**. CCDC numbers (1054664, 1054665, 1054666, 1058370) For ESI and crystallographic data in CIF See DOI:10.1039/b000000x/

molecular ligand L and one molecular metal ion in the CH_3CN/H_2O solution, in which the 1154 peak corresponds to $[Hg_2L_2Cl_3]^+$, the 1013 peak corresponds to $[Ag_2L_2(CF_3SO_3)]^+$, and the 885 peak corresponds to $[Zn_2L_2Cl_3]^+$, respectively (Fig. S1-S3).



Scheme 2 Controllable construction of discrete metallocycles with different conformations.

Whether these three metallocycles, $[Hg_2L_2Cl_4]$, $[Ag_2L_2(CF_3SO_3)_2]$ and $[Zn_2L_2Cl_4]$, have the desired square, rectangular or rhombus conformations as we expected, which one inclines to interlock each other to form catenane. Slowly diffusing the acetonitrile solution of L into the water solution of $HgCl_2$ leads to compound **1**, formulated as $[Hg_2L_2Cl_4]_n$. Compound **1** crystallizes in the space group $C2/c$, where Hg(II) is four-coordinated by two N atoms from two different ligands and two Cl^- anions. As we expected, metallocycle $[Hg_2L_2Cl_4]$ has a similar structure as shown in Scheme 2(b), although it seems a little twist, in which the four sides of metallocycle are equal to 10.48 Å and ∠**CDE** is 103.649°. The lengths of two opposite pyridine rings are 9.596 Å and 10.625 Å, respectively. These metallocycles further interlock each other into a polycatenane chain stabilized by strong π-π interaction from interlocking metallocycles, in which two kinds of above π-π interactions, named **A** (red) and **B** (green), are formed, where the length of **A** is 3.543 Å and the length of **B** is 3.753 Å. The pyridine rings stack in an ***ABAB*** fashion along the polycatenane chain as shown in Fig. 1.

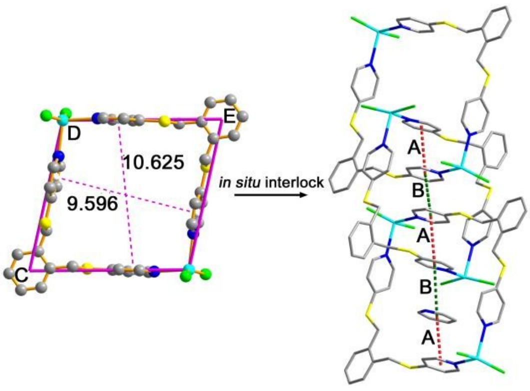


Fig. 1 The process of formation catenane by $[Hg_2L_2Cl_4]$ metallocycle, some bond lengths and angles and ***ABAB*** π-π interaction are marked.

Slowly diffusing the acetonitrile solution of L into the water solution of $AgCF_3SO_3$ leads to compound **2**, formulated as $[Ag_2L_2(CF_3SO_3)_2]$. Single-crystal X-ray analysis reveals that compound **2** is a discrete rectangular metallocycle and has the same topological structure as shown in Scheme 2(a), in which the sides **AB** and **CD** are equal to 4.418 Å, **BC** and **AD** are equal to 13.259 Å; ∠**ABC** is 84.421° and ∠**BCD** is 95.579°.

Slowly diffusion of the acetonitrile solution of L into the water solution of $ZnCl_2$ leads to compound **3**, formulated as $[Zn_2L_2Cl_4]$. Single-crystal X-ray analysis reveals that **3** is crystallized in $P2_1/c$ space group. Each of the Zn^{2+} is four-coordinated by two N atoms from two ligands and two Cl^- anions to form a discrete rhombus metallocycle as shown in Scheme 2(c). The angle ∠**FGH** is 109.46°, and the lengths of the two opposite pyridine rings reduce to 8.793 Å and 10.218 Å compared with those in compound **1** in Fig. 2.

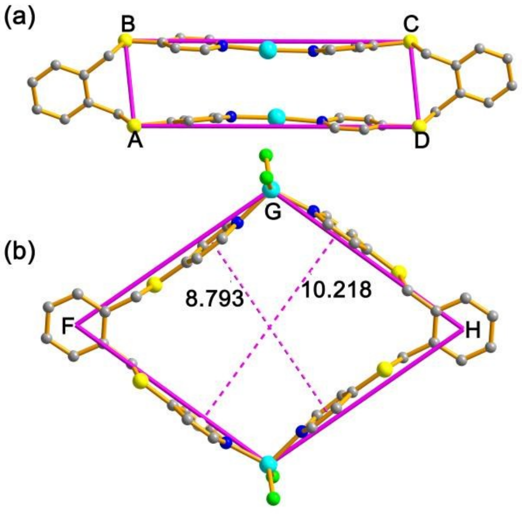
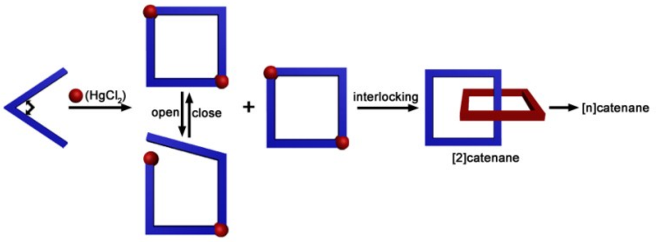


Fig. 2 (a) the $[Ag_2L_2(CF_3SO_3)_2]$ metallocycle. (b) the $[Zn_2L_2Cl_4]$ metallocycle, some bond lengths and angles are marked.

We have found that only square metallocycle $[Hg_2L_2Cl_4]$ can further interlock each other into polycatenane through prolonging reaction time, which are stabilized by strong π-π interaction, while rectangular metallocycle $[Ag_2L_2(CF_3SO_3)_2]$ and rhombus metallocycle $[Zn_2L_2Cl_4]$ cannot overcome such entropically unfavourable process. A possible assembly process of compound **1** is presented in detail (Scheme 3): the ligand L and $HgCl_2$ can assemble into a $[Hg_2L_2Cl_4]$ metallocycle quickly in the CH_3CN/H_2O solution, in which the $[Hg_2L_2Cl_4]$ metallocycle can be opened reversibly and fast. Interlocking of one closed $[Hg_2L_2Cl_4]$ metallocycle with the opened one will lead to a [2]catenane. The interlocking process is slow and can self-correct, in which only the interlocking knots with lowest energy are stable and any other kinetically formed intermediates will be disassociated. Multiple interlocking is more stable than single interlocking, so polycatenanes rather than [2]catenanes are finally isolated in our assembly system.



Scheme 3 A possible assembly process of compound **1**.

Interlocking is an entropically unfavourable process, and it needs suitable interaction to stabilize. In our opinion, the $[Hg_2L_2Cl_4]$ metallocycle prior to interlock into polycatenane may result to their larger cavity and strong *π-π* interaction from neighboring rings; the $[Ag_2L_2(CF_3SO_3)_2]$ metallocycle cannot interlock each other may due to their small cavity. The $[Zn_2L_2Cl_4]$ metallocycle has a larger cavity as $[Hg_2L_2Cl_4]$, however the rhombus cavity seems hard to stack in a favourable form to lead to strong *π-π* interaction. It seems highly interesting that even such a little difference still results to entirely different self-assembly. So we think that suitable cavity and interaction are the key factors governing the interlock from discrete metalloassemblages.

The formation of infinite architectures is very difficult and sensitive; even if using similar anions such as I^- and Br^- anions to replace Cl^- anions, the results are entirely different.[6f] In order to study the effect of anion for the formation of polycatenane, HgI_2 has been selected to replace $HgCl_2$. Slowly diffusing the acetonitrile into DMSO solution of L and HgI_2 for several days leads to compound **4**, formulated as $[Hg_2L_2I_4]_n$. X-ray analysis demonstrates that it contains a polycatenane chain based on square $[Hg_2L_2I_4]$ metallocycle. As shown in Fig. 3, ∠ **C'D'E'** decreases to 103.553° due to the larger corresponding I^- anions compared with Cl^- anions, and the length of **A'** is 3.564 Å, the length of **B'** is 4.032 Å.

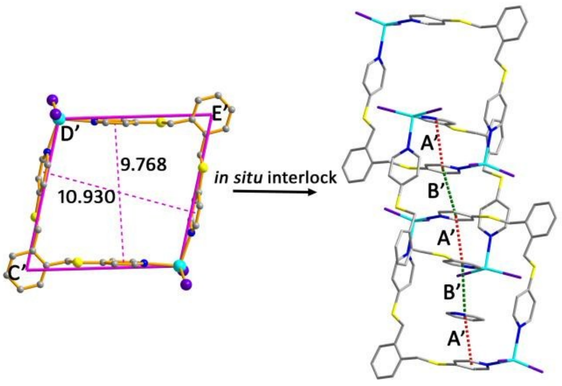


Fig. 3 The process of formation catenane by $[Hg_2L_2I_4]$ metallocycle, some bond lengths and angles and ***A'B'A'B'*** *π-π* interaction are marked.

In conclusion, a novel conformation driven self-assembly system has been developed, where four metallocycles with different conformations have been *in situ* self-assembled. The results indicate that suitable cavity and interaction are the key factors for the formation of polycatenane. Therefore, only square metallocycles can further interlock into a polycatena chain, while rectangular and rhombus metallocycles cann overcome the entropically unfavourable process.

We are thankful for financial support from the 973 Progra (2014CB932101, 2013CB933200), the National Natural Science Foundation of China (21471148, 21131006), "Strategic Priori Research Program" of the Chinese Academy of Sciences (XDA09030102).

Notes and references

1. (a) T. R.Cook, V.Vajpayee, M. H.Lee, P. J.Stang, K. W.Chi, *Acc. Che . Res.*, 2013, **46**, 2464; (b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Ac . Chem. Res.*, 2005, **38**, 369; (c) A. M. Castilla, W. J. Ramsay, J. R. Nitschk , *Acc. Chem. Res.*, 2014, **47**, 2063;(d) M. D. Ward, P. R. Raithby, *Chem. So Rev.*, 2013, **42**, 1619;(e) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Rev.*, 2014, **43**, 1848; (f) L. F. Lindoy, K.-M. Park, S. S. Lee, *Chem. Soc Rev.*, 2013, **42**, 1713; (g) M. J. Hardie, *Chem. Soc. Rev.*, 2010, **39**, 51 Mukherjee, S.; Mukherjee, P. S. T. *Chem. Commun.*, 2014, **50**, 2239;(i) L.Chen, Q.Chen, M.Wu, F.Jiang, M.Hong, *Acc. Chem.Res.*, 2015, **48**, 20 Q. Chen,L. Chen, F. Jiang, M. Hong, *Chem. Rec.* DC 10.1002/tcr.201402095;(k) Y.-F. Han and G.-X. Jin, *Chem. Soc. Res.*, 2014 **43**, 2799.

2. (a) J. F. Ayme; Lux, J.; Sauvage, J. P.; Sour, A., *Chem. Eur. J.*, 2012. 1 5565;(b) R. S. Forgan; Sauvage, J.-P.; Stoddart, J. F., *Chem. Res.*, 2011, **111** 5434;(c) J. E. Beves; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurne , R. T., *Angew. Chem. Int. Ed.*, 2011, **50**, 9260;(d) P. Gavina; Tatay, S., *Current Org. Synth.*, 2010, **7**, 24;(e) M. Beyler; Heitz, V. r.; Sauvage, J.-P., . *Am. Chem. Soc.*, 2010, **132**, 4409;(f) P. C. Haussmann; Stoddart, J. F., *Chem. Rec.*, 2009, **9**, 136;(g) V. Balzani; Credi, A.; Raymo, F. M.; Stoddart, J. I , *Angew. Chem. Int. Ed.*, 2000, **39**, 3348. (h) G. Barin; Coskun, A.; Fouda, M. M.; Stoddart, J. F., *ChemPlusChem.*, 2012, **77**, 159.

3. (a) F. Arico; Badjic, J. D.; Cantrill, S. J.; Flood, A. H.; Leung, K. C.-F., Liu, Y.; Stoddart, J. F., Templated synthesis of interlocked molecules. I *Templates in Chemistry II*, Springer: 2005; pp 203;(b) S. K. Menon; Guha, B.; Agrawal, Y. K., *Rev. Inorg. Chem.*, 2004, **24**, 97;(c) C. Dietrich-Buchecker; Colasson, B.; Fujita, M.; Hori, A.; Geum, N.; Sakamoto, S.: Yamaguchi, K.; Sauvage, J.-P., *J. Am. Chem. Soc.*, 2003, **125**, 5717;(d) . Ibukuro; Fujita, M.; Yamaguchi, K.; Sauvage, J.-P., *J. Am. Chem. Soc.*, 199 , **121**, 11014;(e) F. Aricó; Chang, T.; Cantrill, S. J.; Khan, S. I.; Stoddart, J. F., *Chem. Eur. J.*, 2005, **11**, 4655;(f) E. M. López - Vidal; García, M. D , Peinador, C.; Quintela, J. M., *Chem. Eur. J.*, 2015, **21**, 2259.

4. M. Fujita; Ibukuro, F.; Hagihara, H.; Ogura, K., *Nature* 1994, **367**, 720.

5. (a) R. Zhu; Lübben, J; Dittrich, B.; Clever, G. H., *Angew. Chem.Int. Ed* 2015, **54**, 2796;(b) R. Sekiya; Fukuda, M.; Kuroda, R., *J. Am. Chem. Soc* 2012, **134**, 10987; (c) A. Mishra; Dubey, A.; Min, J. W.; Kim, H.; Stang, P. J.; Chi, K.-W., *Chem. Commun.*, 2014, **50**, 7542;(d) R. Hovorka; Mey - Eppler, G.; Piehler, T.; Hytteballe, S.; Engeser, M.; Topić, F.; Rissanen, K., Lützen, A., *Chem. Eur. J.*, 2014, **20**, 13253; (e) S. Li; Huang, J.; Cook, T. F , Pollock, J. B.; Kim, H.; Chi, K.-W.; Stang, P. J., *J. Am. Chem. Soc.*, 201 **135**, 2084; (f) S. Freye; Hey, J.; Torras - Galán, A.; Stalke, D.; Herbst Irmer, R.; John, M.; Clever, G. H., *Angew. Chem. Int. Ed.*, 2012, **51**, 2191;(V. Vajpayee; Song, Y. H.; Cook, T. R.; Kim, H.; Lee, Y.; Stang, P. J.; Chi, W., *J. Am. Chem. Soc.*, 2011, **133**, 19646;(h) J. J. Henkelis; Ronson, T. K Harding, L. P.; Hardie, M. J., *Chem. Commun.*, 2011, **47**, 6560;(i) S. Sat Morohara, O.; Fujita, D.; Yamaguchi, Y.; Kato, K.; Fujita, M., *J. Am. Chem.*

Soc., 2010, **132**, 3670; (j) J. Lu; Turner, D. R.; Harding, L. P.; Byrne, L. T.; Baker, M. V.; Batten, S. R., *J. Am. Chem. Soc.*, 2009, **131**, 10372;(k) A. Westcott; Fisher, J.; Harding, L. P.; Rizkallah, P.; Hardie, M. J., *J. Am. Chem. Soc.*, 2008, **130**, 2950;(l) M. Fukuda; Sekiya, R.; Kuroda, R., *Angew. Chem. Int. Ed.*, 2008, **47**, 706;(m) M. Beyler; Heitz, V.; Sauvage, J.-P., *Chem. Commun.*, 2008, 5396;(n) T. S. Abedin; Thompson, L. K.; Miller, D. O., *Chem. Commun.*, 2005, 5512;(m) S.-L. Huang, Y.-J. Lin, Z.-H. Li and G.-X. Jin, *Angew. Chem.Int. Ed.*, 2014, **53**, 11218.

6. (a) X. Kuang; Wu, X.; Yu, R.; Donahue, J. P.; Huang, J.; Lu, C.-Z., *Nat.Chem.*, 2010, **2**, 461; (b) Q. Chen; Jiang, F.; Yuan, D.; Lyu, G.; Chen, L.; Hong, M., *Chem. Sci.*, 2014, **5**, 483; (c) Q. Chen; Jiang, F.; Yuan, D.; Chen, L.; Lyu, G.; Hong, M., *Chem. Commun.*, 2013, **49**, 719; (d) S. P. Black; Stefankiewicz, A. R.; Smulders, M. M.; Sattler, D.; Schalley, C. A.; Nitschke, J. R.; Sanders, J. K., *Angew. Chem. Int. Ed.*, 2013, **52**, 5749; (e) L. Jiang; Ju, P.; Meng, X.-R.; Kuang, X.-J.; Lu, T.-B., *Sci. rep.*, 2012, **2**; (f) J. Heine; Schmedt auf der Günne, J. r.; Dehnen, S., *J. Am. Chem. Soc.*, 2011, **133**, 10018;(g) L. Loots; Barbour, L. J., *Chem. Commun.*, 2013, **49**, 671;(h) C.-M. Jin; Lu, H.; Wu, L.-Y.; Huang, J., *Chem. Commun.*, 2006, 5039;(i) Z. Yin; Zhang, Y.; He, J.; Cheng, J.-P., *Chem. Commun.*, 2007, 2599.

7. (a) G. J. E. Davidson and S. J. Loeb, *Angew. Chem. Int. Ed.*, 2003, **42**, 74; (b) V. N. Vukotic, K. J. Harris, K. Zhu, R. W. Schurko and S. J. Loeb, *Nat.Chem.*, 2012, **4**, 456; (c) K. Zhu, V. N. Vukotic, C. A. O'Keefe, R. W. Schurko and S. J. Loeb, *J. Am. Chem. Soc.*, 2014, **136**, 7403; (d) D. J. Mercer, V. N. Vukotic and S. J. Loeb, *Chem. Commun.*, 2011, **47**, 896; (e) L. K. Knight, V. N. Vukotic, E. Viljoen, C. B. Caputo and S. J. Loeb, *Chem. Commun.*, 2009, 5585.