View Article Online View Journal

# ChemComm

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: N. Liu, S. Huang, X. Liu, H. Luo and T. S. A. Hor, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC08009C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm



Journal Name

# COMMUNICATION

# Self-assembled [2]Catenane in Trapezodial Metallacycles with [Cp\*Ir]-Corner

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

Naifang Liu,<sup>ab</sup> Sheng-Li Huang,<sup>\*a</sup> Xiaogang Liu,<sup>ab</sup> He-Kuan Luo<sup>\*a</sup> and T. S. Andy Hor<sup>\*abc</sup>

DOI: 10.1039/x0xx00000x

www.rsc.org/

A series of trapezoidal metallacycles were synthesized by the selective combination of a rigid with a flexible arm. The [2] catenane 3 was obtained by self-assembly when the cavity size of the trapezodial rings is optimised.

Interlocked superstructures are of topical interest, as demonstrated by the molecular machines created by Sauvage, Stoddart, Feringa and others.<sup>1</sup> Catenanes as entangled architectures are particularly well suited as designer molecular devices that exploit the dynamics of the interlocked molecules. As visually appealing they are, their syntheses still pose great technical challenges due to the complex and constrained topologies.<sup>2</sup>

The first synthesis of [2]catenane in 1960<sup>3</sup> was readily followed by a variety of interlocked superstructures largely attributed to the development of two effective synthetic routes: template and self-assemble methods.<sup>2</sup> The former can provide obvious driving force responsible for catenation,<sup>4</sup> whereas the latter, which is biomimetic in nature, is versatile but more difficult to control the delicate intermolecular interactions. Although several self-assembled molecular topologies, such as, catenanes,<sup>2</sup> Solomon links,<sup>5</sup> Borromean rings,<sup>6</sup> interlocked cages<sup>7</sup> and knots<sup>8</sup> have been reported, most of them are almost serendipitously obtained from the metallasupramolecule synthesis.9 Inter-balance of many influencing factors is spontaneous and complex thus difficult to decipher or control.

Owing to its comparatively simple topology, the [2]catenane, the simplest type of catenane with Hopf link topology,

candidates in exploring the spontaneously interlocking process.<sup>2</sup> The C<sub>2</sub> symmetry of [2]catenane provides a suitable template for C<sub>2</sub> macrocycle with a single interlock. One typical C<sub>2</sub> symmetric ring is trapezoidal metallacycle (Fig. 1), which was obtained by combining three components of cis-protected Pd-corner and two types of bifunctional pyridyl ligands; it however suffers from concurrent formation of other thermodynamic products.<sup>10</sup> Contrary to palladium, [Cp\*Ir]based corners each holding three available coordination sites, viz. a bis-chelating linker and a monodentate bifunctional linker are needed to satisfy the requirements of coordination saturation and cyclic structural formation.<sup>11</sup> In contrast to monodentate coordination interaction, the bonding energy of chelating metal-ligand interaction has a geometric growth, that decreases the possibility of the cleavage and re-bonding of coordination bonds. Harness of the chelate effect can simplify the formation and ease isolation in suppressing minimal single linker assemblies. This shifts the attention to judicious selection of bis-chelating linker as the interpenetration outcome is sensitive to its length, spacer and aromaticity.<sup>6</sup> Tetrapyrido[3,2-a:2',3'-c:3",2"-h:2"',3"'j]phenazine (tpphz) L'1 and 9,11,20,22-tetraaza-





hemComm Accepted Manuscript

Published on 07 November 2017. Downloaded by University of Newcastle on 08/11/2017 01:52:48.

<sup>&</sup>lt;sup>a</sup> Institute of Materials Research and Engineering, A\*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634. Singapore. E-mail: huangsl@imre.a-star.edu.sg; luoh@imre.astar.edu.sg.

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, Faculty of Science, National University of Singapore, 3 Science, Drive 3, Singapore, 117543, Singapore.

<sup>&</sup>lt;sup>c.</sup> Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong. E-mail: andyhor@hku.hk.

<sup>+</sup>Electronic Supplementary Information (ESI) available: Synthesis procedure and characterisation data, including NMR spectra, ESI-MS spectra and X-ray data. CCDC 1549351. See DOI: 10.1039/x0xx00000x

### COMMUNICATION

Published on 07 November 2017. Downloaded by University of Newcastle on 08/11/2017 01:52:48.

tetrapyridopentacene (tatpp)  $L^{l}_{2}$ , which are long and rigid aromatic bridging linker, may provide potential supramolecular recognition sites for  $\pi$ - $\pi$  stacking interactions.<sup>12</sup>

The combination of [Cp\*Ir]-corner and bis-chelating linker  $L_n^I$  easily offered the linear arm with two available coordination sites, in order to form the trapezoidal metallacycle, one flexible monodentate bifunctional linker is the best choice. The methylene unit is widely utilized in the design of flexible ligands,<sup>13</sup> and this prompted us to design a series of bifunctional ligands  $L_n^{II}$  that include the terminal pyridyl groups with free-to-rotate methylene. Both the length of the central backbone and terminal pyridyl groups could then be tuned to influence the interpenetrating process (Scheme 1).

The flexible ligand  $L_{1}^{II}$  has been successfully employed in the Pd-based [2]catenane synthesis.<sup>10b</sup> In contrast, treatment of  $Cp*Ir-L_1'$  with  $L_1''$  produced non-interlocked structure 1, that was confirmed by NMR spectroscopy and Electrospray Ionisation Mass Spectrometry (ESI-MS). NMR is used to evaluate the interpenetration outcome, as a very high upfield shift of the central aromatic proton signals caused by mutual shielding between the two component rings would be diagnostic for the catenane formation. The methylene protons of  ${\bf 1}$  appear at 5.17 ppm and all the aromatic protons are above 7.10 ppm, indicating no upfield shift. ESI-MS analysis could also be used to monitor the interlocking process. Although the even-cation of dimeric structure has same MS peaks with one corresponding odd-cation of monomeric structure, the odd-cation peak of dimeric structure is unique. The isotopic distributions are an unambiguous indication of the exact mass of the MS fragment, that also allow distinguishing between the dimeric and monomeric structure. The mass spectrum of 1 showed relevant peaks at m/z= 1834.3,

L۳,

L".

Scheme 1 The chemical structures of Ir-L<sup>I</sup><sub>n</sub>-Ir arms and the

flexible monodentate bifunctional linker L<sup>"</sup>n.



The locking process from monomeric rings to catenated dimers must be accompanied by the distribution decrease and symmetry increase of the whole system. In [2]catenane formation, the binding energy between two independent rings must be sufficient to cover the entropy cost. Enhancing ring-ring interactions could increase the possibility of interlocking. For  $L^{II}_{2}$ , its failure to form interlocked structure may be explained by poor ring-ring interactions due to lengthy terminal pyridyl groups (Fig. 2). This postulate was tested and





DOI: 10.1039/C7CC08009C

Journal Name

Published on 07 November 2017. Downloaded by University of Newcastle on 08/11/2017 01:52:48.

## Journal Name

confirmed by the use of  $L_{3}^{"}$ , which resulted in the absence of interlocked structure or monomeric ring under a range of terminal pyridyl groups. Appling the same synthetic method to 1 and 2, we were unable to find any evidence of mono-ring formation through either NMR or MS analysis, suggesting that the trapezoidal ring with enlarged cavity is unstable for formation.

Compared to  $L_{1}^{"}$ ,  $L_{2}^{"}$  and  $L_{3}^{"}$ , the ligand  $L_{4}^{"}$  has mediumlength backbone and shorter terminal pyridyl groups, which should generate enough ring-ring interactions to balance the entropy expense in the catenane formation. Mix of an equimolar of  $Cp^*Ir-L_1^I$  and  $L_4^{II}$  in MeOH at r.t. resulted in pure light-yellow solids of [2]catenane complex 3 upon isolation. In contrast to the <sup>1</sup>H NMR spectra of 1 and 2, the protons of phenylene and methylene of  $L^{II}_{4}$  moieties are significantly shifted upfield, which is diagnostic of interlock of the two rings. Further, evidence for [2]catenane 3 formation was obtained through ESI-MS analysis (Fig. S16). The mass spectrum of a dilute solution of 3 revealed peaks at m/z=1165.6, which corresponds to the ion [**3**-3OTf]<sup>3+</sup>. The isotopic distributions for the peaks of the corresponding ions were consistent with simulated distributions (Fig. 3).  $L_{5}^{"}$  has similar structure as  $L_{4}^{"}$ but atomic link between methylene and central backbone is nitrogen replacement of carbon. Although the positive sites are located at the terminal of central backbones, the positive charge could also transfer to the central site thus creating positive charge repulsion when two central backbones meet. The replacement of  $L_{5}^{"}$  with  $L_{4}^{"}$  led to the non-interlocked structure 4 as expected (Fig. S19-S21). Besides the influence of flexible linker, the influence of bis-chelating linker was also investigated. The treatment of  $Cp^*Ir-L_1^I$  and  $L_4^{II}$  gave







DOI: 10.1039/C7CC08009C

COMMUNICATION

[2] catenane **3**, but the combined use of  $Cp^*Ir-L_2^I$  and  $L_4^{II}$ produced a mono-ring 5 (Fig. S23-S24). The reason of unlocking may be similar to the formation of mono-ring 1 - the extension of one parallel side of trapezoid leads to a decreased ring size which does not favour interpenetration.

By the Le Chatelier's principle, when a system at equilibrium is subjected to change in concentration, the system readjusts itself to counteract the effect of the applied change. The equilibrium mixture of non-interlocked and interlocked assemblies is disrupted following concentration change due to the dynamic behaviour of metal-ligand interaction and weak binding between independent individuals in interlocked metallasupramolecules.<sup>10b,14</sup> Accordingly, higher concentration could favour the interlocking path, whereas lower concentration could weaken such potential. This phenomenon was observed in the combination of  $Cp^*Ir-L_1^{I}$  and  $L_4^{II}$  with variable concentrations. At high concentrations (0.1 mM, with respect to Cp\*Ir), [2]catenane 3 is the exclusive product. At medium concentration (0.04 mM), the equilibrium mixture of interlocked- and non-interlocked was observed. Only the mono-ring 3' was found at low concentrations (0.005 mM). This concentration-dependent dynamic system is illustrated through NMR spectra changes (Fig. 4).

In summary, we have designed and synthesized a series of trapezoidal metallacycles of Cp\*Ir bearing one rigid bischelating linker and one flexible bifunctional pyridyl linker. Optimal shape and size of the trapezoidal metallacycles are critical for interlocking. The results showed that overly small ring cannot provide sufficient space for interlocking, and enlarged ring cannot create efficient ring-ring interaction with poor structural stability. Only with optimal ring sizes can favour interlocking through sufficient compensation of entropy cost by binding energy of the two independent rings. This points to the central importance of intermolecular interaction

DOI: 10.1039/C7CC08009C

in governing the interlocking assembly in the formation of [2]catenane structure. We are currently investigating other factors especially supplementary hydrogen bonding and metal-metal interactions.

We acknowledge IMRE-A\*STAR for infrastructure support and financial assistance (IMRE/14-1C0120). Technical support from staff at CMMAC of NUS Department of Chemistry is also appreciated.

### Notes and references

Published on 07 November 2017. Downloaded by University of Newcastle on 08/11/2017 01:52:48.

- 1 D. A. Leigh, Angew. Chem. Int. Ed., 2016, **55**, 14506–14508.
- 2 (a) M. Fujita and K. Ogura, Coord. Chem. Rev., 1996, 148, 249-264; (b) M. Fujita, Acc. Chem. Res., 1999, 32, 53-61; (c) N. H. Evans and P. D. Beer, Chem. Soc. Rev., 2014, 43, 4658-4683; (d) G. Gil-Ramírez, D. A. Leigh and A. J. Stephens, Angew. Chem. Int. Ed., 2015, 54, 6110–6150; (e) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, Angew. Chem. Int. Ed., 2011, 50, 9260 9327.
- 3 E. Wasserman, J. Am. Chem. Soc., 1960, 82, 4433-4434.
- 4 T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.*, 2000, **200-202**, 5-52.
- 5 (a) C. Schouwey, J. J. Holstein, R. Scopelliti, K. O. Zhurov, K.
  O. Nagornov, Y. O. Tsybin, O. S. Smart, G. Bricogne, K. Severin, *Angew. Chem. Int. Ed.*, 2014, **53**, 11261–11265; (b)
  Y. H. Song, N. Singh, J. Jung, H. Kim, E. H. Kim, H. K. Cheong, Y. Kim, K. W. Chi, *Angew. Chem. Int. Ed.*, 2016, **55**, 2007–2011.
- 6 (a) S. L. Huang, Y. J. Lin, T. S. A. Hor, G. X. Jin, J. Am. Chem. Soc., 2013, 135, 8125–8128; (b) S. L. Huang, Y. J. Lin, Z. H. Li, G. X. Jin, Angew. Chem. Int. Ed., 2014, 53, 11218–11222; (c) T. Kim, N. Singh, J. Oh, E. H. Kim, J. Jung, H. Kim, K. W. Chi, J. Am. Chem. Soc., 2016, 138, 8368–8371; (d) L. Zhang, L. Lin, D. Liu, Y. J. Lin, Z. H. Li, G. X. Jin, J. Am. Chem. Soc., 2017, 139, 1653–1660.
- 7 M. Frank, M.D. Johnstone, G.H. Clever, Chem. Eur. J., 2016, 22, 14104-14125.
- 8 K. E. Horner, M. A. Miller, J. W. Steed, P. M. Sutcliffe, *Chem. Soc. Rev.*, 2016, **45**, 6432-6448.
- S. L. Huang, T. S. A. Hor, G. X. Jin, Coord. Chem. Rev., 2017, 333, 1-26.
- 10 (a) M. Fujita, M. Aoyagi, F. Ibukuro, K. Ogura, K. Yamaguchi, J. Am. Chem. Soc., 1998, **120**, 611–612; (b) S. Prusty, S. Krishnaswamy, S. Bandi, B. Chandrika, J. Luo, J. S. McIndoe, G. S. Hanan, D. K. Chand, Chem. Eur. J., 2015, **21**, 15174– 15187.
- (a) S. L. Huang, T. S. A. Hor, G. X. Jin, Coord. Chem. Rev., 2017, 346, 112-122; (b) Y. F. Han, G. X. Jin, Acc. Chem. Res., 2014, 47, 3571-3579; (c) Y. F. Han, W. G. Jia, W. B. Yu, G. X. Jin, Chem. Soc. Rev., 2009, 38, 3419; (d) Z. J. Yao, W. B. Yu, Y. J. Lin, S. L. Huang, Z. H, Li, G. X. Jin, J. Am. Chem. Soc., 2014, 136, 2825–2832; (e) H. Li, Y. F. Han, Y. J. Lin, Z. W. Guo, G. X. Jin, J. Am. Chem. Soc., 2014, 136, 2982–2985.
- (a) A. Wragg, M. R. Gill, C. J. Hill, X. D. Su, A. J. H. M. Meijer, C. Smythe, J. A. Thomas, *Chem. Commun.*, 2014, **50**, 14494--14497; (b) S. Liu, H. Liang, K. Y. Zhang, Q. Zhao, X. Zhou, W. Xu, W. Huang, *Chem. Commun.*, 2015, **51**, 7943--7946; (c) Y. J. Cho, S. Y. Kim, M. Cho, K. R. Wee, H. J. Son, W. S. Han, D. W. Cho, A. O. Kang, *Phys. Chem. Chem. Phys.*, 2016, **18**, 15162--15169; (d) M. J. Kim, R. Konduri, H. Ye, F. M. MacDonnell, F. Puntoriero, S. Serroni, S. Campagna, T. Holder, G. Kinsel, K. Rajeshwar, *Inorg. Chem.*, 2002, **41**, 2471-2476; (e) W. Guo, S. O. Obare, *Tetrahedron Lett.*, 2008, **49**, 4933-4936.
- 13 (a) M. Fujita, F. Ibukuro, K. Yamaguchi, K. Ogura, J. Am. Chem. Soc., 1995, 117, 4175–4176; (b) M. Fujita, F. Ibukuro,

H. Seki, O. Kamo, M. Imanari, K. Ogura, J. Am. Chem. Soc., 1996, **118**, 899–900.

14 N. Singh, D. Kim, D. H. Kim, H. Kim, E. H. Kim, M. S. Lah, K. W. Chi, *Dalton Trans.*, 2017, **46**, 571-577.



Table of contents entry

