

Self-Assembly of Molecular Borromean Rings from Bimetallic Coordination Rectangles**

Sheng-Li Huang, Yue-Jian Lin, Zhen-Hua Li, and Guo-Xin Jin*

Dedicated to Professor Li-Xin Dai on the occasion of his 90th birthday

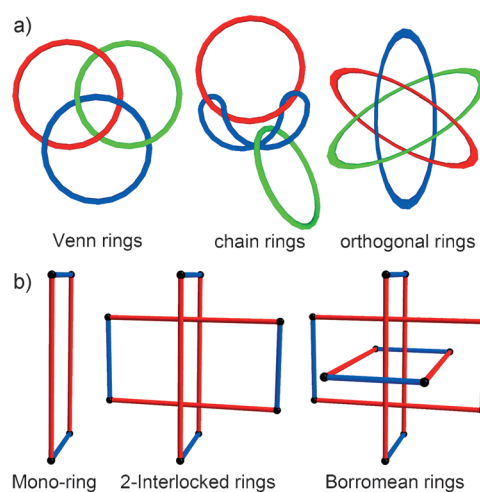
Abstract: In contrast to conventional stepwise synthesis of molecular Borromean rings, a self-assembly synthetic method which proceeds without the aid of a template has been developed. In the formation of molecular rectangles, by adjustment of the long-arm length of the rectangles, a series of size-dependent Borromean-link frameworks were constructed. Both the shortest length of two arms and the relative proportion of the length of the long arm to that of the short arm play a key role in the formation of Borromean rings. DFT calculations were used to provide theoretical support for the formation of discrete interlocked frameworks.

Interest in interlocked molecular species is rapidly growing not only because of their intriguing structures^[1] and topological importance,^[2,3] but also because of their potential applications as smart materials and nanoscale devices.^[4] One fascinating and challenging synthetic target comprising entangled bodies is the molecular Borromean link.^[5,6] Such a molecule comprises three macrocycles combined such that none of the two-body subsystems are linked, yet collectively they form an inseparable ensemble. The aesthetic beauty of the assembly, which has led to attempts to synthesize this nontrivial link, is a formidable challenge generated from its topological complexity. In 1997, the first artificial species was constructed from single-stranded DNA by Seeman and co-workers.^[7] Two years later, a ring-in-ring strategy was proposed by Busch and co-workers.^[8] In 2004, Stoddart developed an all-in-one approach which facilitated the assembly of Borromean rings^[9] and upon demetalation led to metal-template-free Borromean rings.^[10] All these reported examples demonstrate the stepwise synthesis with the aid of a well-known driving force, such as a donor–acceptor interaction and metal templation.^[11,12] Nevertheless, the spontaneous assembly of discrete Borromean species remains unexplored. As was predicted by Walba, “Certainly one day molecular Borromean rings will be created by a directed

approach”,^[13] however, this is an as-yet unrealized goal and a challenge we have taken up in our laboratories.

Self-assembly provides a facile means for achieving ordered architectures from functional building blocks, and can considerably reduce synthetic costs and result in a single thermodynamic product in high yield.^[14–16] Because of the highly directional and easily accessible nature of coordination bonds, coordination-driven self-assembly is regarded as an efficient tool in the synthesis of well-defined architectures ranging from multidimensional frameworks^[17–19] to discrete species.^[20–22] The coordination-driven self-assembly of interlocked metallasupramolecules is a highly topical area of current research,^[12,23] in particular, many catenated dimers have been reported.^[24] Recently, we reported a surprising observation that enlarging just one arm of a metallarectangle led to the isolation of trimeric complexes with Borromean-link structures.^[25] For self-organized interlocked species, the cause of formation and nature of the driving force is a complicated and perplexing question. The desire to understand the interpenetrating action and to provide theoretical support for further construction of interlocked species motivates these studies, including those on the design, synthesis, characterization, and theory of interlocked molecular architectures, specifically, the Borromean link.

There are three principal representations of the Borromean link: Venn rings,^[26] chain rings,^[27] and orthogonal rings (Scheme 1 a).^[5] The orthogonal rings consist of three mutually perpendicular rings and feature three-dimensional symmetry and easy self-assembly, for example, its most accessible



Scheme 1. a) Three representations of the molecular Borromean link. b) The noncatenane n -interlocked rectangles ($n = 2$ or 3).

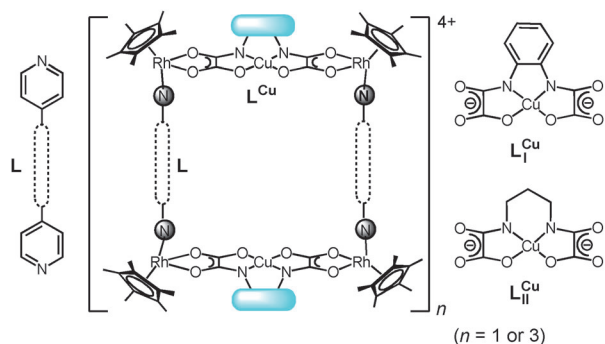
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construction is by a metal-template assembly.^[9,10] The size-dependent molecular Borromean rings recently observed by our group also belong to the orthogonal rings grouping, therefore we continue to investigate this synthetic Borromean link by coordination-driven formation of rectangles, a potentially general method. The discrete rectangular complexes hold two varying linkers, which not only satisfy the space requirement for noncatenane interlocked structures, but also offers more flexibility in regulating the length.^[25,28] The rectangular complex should be the ideal model to understand molecular Borromean rings, even in terms of the nature of interpenetration.

Herein, we present a self-assembly approach to synthesizing molecular Borromean rings based on rectangular complexes, with components of [Cp*Rh] (Cp* = η^5 -C₅Me₅), the bis(chelating) metallaligands **L**^{Cu}, and bifunctional pyridine derivatives **L** (Scheme 2). Based on the coordination-driven self-assembly, the metal-corner strategy is one of the most popular approaches for the synthesis of molecular rectan-



Scheme 2. Structural representation of the metallarectangles as well as metallaligands **L**^{Cu} used in the synthesis of these cycles.

gles.^[29] Herein, the metal-corner [Cp*Rh] fragment offers three available coordination sites. To meet the desired coordination number and to form a cycle, one bis(chelating) ligand and another bifunctional pyridine derivatives are needed.^[30] The two types of arms (spacers) are joined at the metal corners to give the rectangular architectures. In principle, the selection of the short-arm spacer ligand is very important to the formation of molecular Borromean rings. Here, in the beginning, the molecular precursor **L**₁^{Cu} [**L**₁^{Cu} = {Cu(opba)}²⁺; opba = *o*-phenylenebis(oxamato)] was used as the short bis(chelating) linker based on their suitable length and open copper center. A series of pyridine derivatives (Figure 1) were used as the longer monodentate bifunctional linkers. On the basis of the size-dependent Borromean-link phenomenon, we were interested in determining whether Borromean-link structures also could be observed when much longer pyridine linkers were introduced. Furthermore, we wanted to explore the formation mechanisms of molecular Borromean rings.

All of the complexes prepared comprise [4Rh+2Cu] nuclear metallarectangles with different component units. Therein, the three remaining coordination sites of half-sandwich rhodium fragments were occupied by the pyridyl

donor **L** and the chelating ligand **L**₁^{Cu}. The Cu^{II} center has an approximate square-pyramidal coordination with two nitrogen and two oxygen atoms from the opba group in the equatorial plane. The length of copper-containing arms **L**₁^{Cu} is about 10.6 Å. Nevertheless, the lengths of the pyridyl arms change significantly from 7.0 to 24.1 Å (Figure 1). The

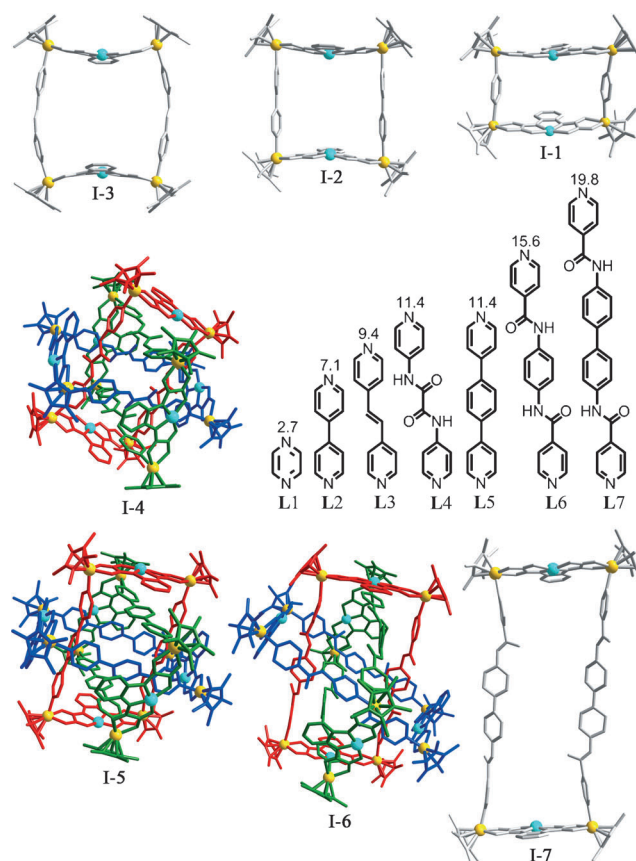


Figure 1. The size-dependent Borromean rings and single-crystal X-ray structures of **L**₁^{Cu}-based complexes **I-1-I-7**,^[34] and chemical structure of the pyridyl arms.

complexes are monomeric rings when the pyridyl arms are shorter than 15.6 Å (**I-1**, pz = 7.0 Å; **I-2**, bpy = 11.3 Å; **I-3**, bpe = 13.3 Å). However, upon lengthening the pyridyl arms through the use of the longer linker dpo, the Borromean-link complex **I-4** was obtained. The three interpenetrating, but noncatenated rectangles make up an inseparable ensemble with each ring threading through one of the other rings and threaded by the other one (1→2, 2→3, 3→1), wherein scission of any one of the rings destroys the union of the three rings (Figure 1). It is noteworthy that there are many observable interactions between different rings, such as hydrogen bonds and Cu⋯O interactions (see Figure S15 in the Supporting Information), and these interactions may affect the formation of the trimeric structure. To ascertain if the formation of the Borromean-link structure is determined by weak interactions or just by the longer pyridyl arms, the ligand bpb, with a nearly equivalent N⋯N distance but without obvious functional groups, was tested. The resulting

complex **I-5** also had a Borromean-link structure like **I-4**, and indicated that the length of the pyridyl arms may be more important in the assembly of Borromean rings. Nevertheless, we sought to investigate whether merely using pyridyl arms longer than bpe is enough for Borromean ring formation, or whether the length of pyridyl arms should be restricted to a certain range. Therefore, a linker (bpfb) which is much longer than dpo (or bpb) was used, and we were surprised to observe that the bpfb linker also resulted in the formation of the trimeric framework **I-6**. Similar to the case of **I-4**, there were strong interactions between the carbonyl groups of bpfb and the open copper centers of the short arms (see Figure S16). Moreover these were found to be even stronger than the Cu...O interactions existing in **I-4**. Although we speculate that the length of the pyridyl arms should be restricted to a certain range for the construction of Borromean rings, this cannot be unequivocally proven without reaching the upper limit. In an attempt to reach this limit, an extremely long ligand was needed, and we choose bpfp. As expected, **I-7** was found to be a monomeric rectangle. Because of the large inner-space of **I-7**, one additional bpfp ligand was found to coordinate with the open copper center inside the short arms (see Figure S17), which occupied the cavity of rectangle and presumably stabilized the arrangement.

As mentioned above, the selection of the short-arm linker is very important to form molecular Borromean rings. By using L_1^{Cu} as short arm, a series of size-dependent Borromean rings were synthesized. The ligand L_n^{Cu} [$L_n^{Cu} = \{Cu(pba)\}^{2-}$; pba = 1,3-propylenebis(oxamato)] also has open copper centers and is of a similar length to that of L_1^{Cu} , but with less aromatic properties. With the use of L_n^{Cu} in the place of L_1^{Cu} , similar results were obtained. These complexes are monomeric rings when the pyridyl arms are shorter than 15.62 Å (**II-1**, pz; **II-2**, bpy; **II-3**, bpe), but the Borromean-link complex **II-5** is obtained when bpb was used (Figure 2). This phenomenon offers further evidence that in the self-assembly of metallarectangles, a suitable long-arm length may lead to the isolation of molecular Borromean architectures.

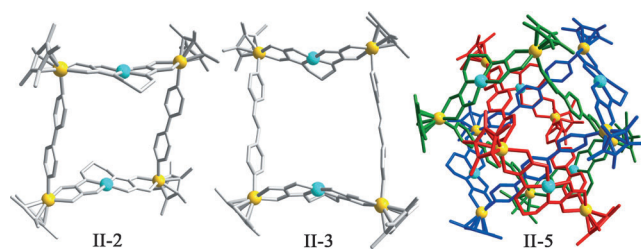


Figure 2. The single-crystal X-ray structures of L_n^{Cu} -based complexes.^[34]

In the assembly of such molecular rectangles, the enlarged pyridyl arms create void space inside the rings as the arms become longer, and may introduce instability in the complexes. To confirm the active void space of **I-2**, *p*-carborane (*p*-CB) was introduced as a guest molecule and resulted in the formation of complex **I-2a** (*p*-CB ⊂ **I-2**; see Figure S11). For the sake of probing the importance of Cu...O interactions in the formation of the trimeric structures **I-4** and **I-6**, sodium *p*-

toluenesulfonate (NaTs) was included to inhibit intramolecular Cu...O interactions between the rectangles with the expectation to obtain monomeric rectangles instead of the trimeric structures. By applying this method, the expected bpfb-bridged monomer **I-6a** was obtained (see Figure S13). Nevertheless, with regard to the dpo-bridged complex, the trimeric complex **I-4a** was obtained with just the change of one of the OTf[−] (Tf = O₂SCF₃) anions as guest inside its cavity (see Figure S12). The Cu...O interaction thus appears to determine the formation of bpfb-bridged trimeric frameworks. In contrast, compared with the Cu...O interaction, other interactions (e.g., π-π stacking) are obviously more important in the formation of the dpo-bridged trimer because of the dpo arm having a more favorable length than the bpfb arm.

Herein, by using dpo as a long-arm linker, both L_1^{Cu} and L_n^{Cu} can provide Borromean-link structures. In previously reported results, only the monomeric rectangle **E-1** was obtained when the bis(chelating) linker was replaced by oxalate (see Figure S18).^[31a] By using the longer short-arm linker dhnd (H₂dhnd = 6,11-dihydroxy-5,12-naphthacenedione), another monomeric rectangle (**E-2**) was also obtained (see Figure S19). This observation provides powerful proof that insufficient length of the short arm can prohibit formation of the Borromean rings. Surprisingly, by using the same dhnd linker, but a longer long-arm linker such as dbd [dbd = 1,4-di(pyridin-4-yl)buta-1,3-diyne], the noncatenane 2-interlocked complex **E-3** was obtained (see Figure S20).^[32] The structural changes from monomer to dimer should be caused by the thinner spacer dbd, not its additional length.

By combining all the data (see Table S2), a relationship between long/short-arm and *n*-interlocked rectangles was determined (Figure 3). To form noncatenane *n*-interlocked rectangles, three criteria are necessary: 1) the short arms need to be long enough to accommodate the spatial requirements of the long arms; 2) the long arms need to be long enough to accommodate the entire length of the short arms; 3) the ratio of the length of the long arm to that of the short arm should be appropriate for the production of ring–ring interactions. Furthermore, the application of a long-arm linker with

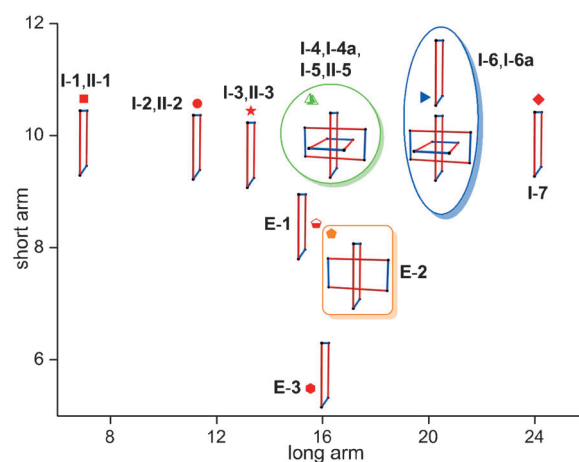


Figure 3. The *n*-interlocked rectangular structures determined by the length of short and long arms [Å].

a slim spacer (e.g., alkyne triple bond) could give surprising results.

In an ideal Borromean-link system, the dihedral angles between two planes should be 90°, but the dihedral angles deviate slightly from the model 90° in the herein-reported Borromean-link systems (see Table S1). The dihedral angles (see Figure S23) in **I-5** are the closest to 90°. Although the length of the long-arm linkers in **I-4** and **I-5** are nearly equivalent, **I-4** shows significantly different dihedral angles (see Figure S21) from those in **I-5**, the largest angular difference being 5.6°. Interestingly, the dihedral angles in **I-4a** are much larger than those in **I-4** and almost equivalent to those of **I-5**. The changes indicate that the encapsulation of OTf[−] will strengthen the aromatic property of the trimeric system and add stability to this framework. The dihedral angles (see Figure S24) in **I-6** were found to deviate the most from 90°, and may be due to its self-adjusting action brought about by the large difference in the length of the long- and short-arm linkers. Surprisingly, the dihedral angles in **II-5** (see Figure S25) have the same values. In all the Borromean rings described herein, the three individual monomeric rings have the same symmetric center, and indicate that all three monomeric rings holding the same symmetric center still is the foundation of Borromean systems.

In support of the solid-state structures as evidenced from the X-ray diffraction analysis, the electrospray ionization mass spectrometry (ESI-MS) data for **I-4**, **I-5**, **I-6**, and **II-5** also point to the same species as their trifluoromethanesulfonate salts in solution. Signals for the parent complexes minus their counteranions were observed: [**I-4**−3OTf]³⁺ (*m/z* 2507.65, see Figure S27), [**I-5**−3OTf]³⁺ (*m/z* 2487.70, see Figure S28), [**I-6**−3OTf]³⁺ (*m/z* 2659.71, see Figure S29), and [**II-5**−3OTf]³⁺ (*m/z* 2419.39, see Figure S30). This data strongly suggests that not only the rectangular structures but also the Borromean-link frameworks remain intact in solution. The mass peaks obtained experimentally were all isotopically resolved and in good agreement with their theoretical distributions. The ESI-MS and crystal structures of **I-4**, **I-5**, **I-6**, and **II-5** provide collective proof for the formation of these Borromean-link structures by self-assembly, and their existence in both solution and the solid state.

As we know, compared with monomeric rings, the formation of *n*-interlocked rings must be accompanied by entropy reduction because of the distribution decrease and symmetry increase of the whole system. Because of the thermodynamically favorable character of [Cp*Rh]-based coordination frameworks, the interactions between adjacent arms play a key role in the formation of interpenetrating frameworks. Here, we performed binding energy calculations to investigate the driving force to form *n*-interlocked rings (see Table S3). First of all, although we did not observe the existence of a bpe-bridged trimeric complex experimentally, a bpe-bridged Borromean ring was built computationally (see Figure S31) and its geometry was fully optimized. The binding energy is defined as the energy gained in forming the trimer from three monomeric rectangles. Given that forming the trimer from monomers is an entropy-decreasing process, the small energy gain of −14.53 kcal mol^{−1} to form the bpe-bridged trimer is not enough to overcome the entropy loss

and thus no bpe-bridged trimer was formed. The calculation results showed that the binding energy between the three bpb-bridged monomeric rectangles in **I-5** (−63.88 kcal mol^{−1}) is much stronger than that between the three monomeric rings in the bpe-bridged hypothetical trimer. The driving force to form **I-5** is the π – π stacking interaction between π systems of the long- and short-arm linkers. The difference between bpe-arm and bpb-arm linkers is that the middle benzene ring of the bpb arm is substituted by ethylene. To form the π – π stacking interaction, the distance between the two planes of the two π systems should adopt an optimal distance of around 3.4 Å for a parallel-displaced benzene dimer.^[33] However, after the replacement of the benzene ring with ethylene, the distance between the long-arm linker decreases from around 16.3 Å to 14.2 Å in the monomeric rectangle. This decrease leads to a smaller distance between the long- and short-arm linkers in the bpe-bridged hypothetical trimer, and decreases from around 3.2 Å to 2.1 Å. For **I-4**, the formation of Cu⋯O interactions between the long- and short-arm linkers provides extra binding energy (−66.65 kcal mol^{−1}). If the benzene ring is replaced by a −CONH−C₆H₄−NHCO− unit, although the increase of the distance between the long arm and the short arm in **I-6** disfavors the formation of the trimeric structures, as it weakens the π – π stacking interaction between the long and short arms, our simulation indicates that the additional Cu⋯O interactions are also very important to stabilize the trimer (−65.95 kcal mol^{−1}). In **I-6**, the cross-rings largely deviate from perpendicularity to ensure that the long and short arm have suitable binding distance. The ligand 1,4-bis[2-(4-pyridyl)ethenyl]benzene (bpeb) has a nearly equivalent N⋯N distance as the bpfb linker, but the binding energy of bpeb-bridged hypothetical trimer was calculated to only be −2.54 kcal mol^{−1}. This value is much smaller than that for the bpfb-bridged complex, and may be ascribed to the long distance and missing functional groups of bpeb linker. Hence, we may arrive at the conclusion that for the *n*-interlocked complexes, the binding energy between different rings is very important. No inter-ring interactions result in formation of **I-3** and bpeb-bridged monomeric rings. By comparison, the π – π stacking and Cu⋯O interactions respectively favor the formation of the trimeric complexes **I-4**, **I-5**, and **I-6**. The ΔG value is an important parameter to evaluate whether a reaction can occur, and should be less than zero for a spontaneous reaction. In the process of three monomeric rings forming one trimer, the ΔS value is about −182.8 cal mol^{−1} K^{−1} at 298 K. By the Gibbs free energy calculation, the corresponding ΔG values for going from monomeric rings to a Borromean ring are 39.94 (bpe-bridged), −12.18 (dpo-bridged), −9.41 (bpb-bridged), −11.46 (bpfb-bridged), and 51.93 kcal mol^{−1} (bpeb-bridged). These calculated results agree well with the experimental results, as indicated by the ΔG value for forming the bpe-bridged Borromean ring is greater than zero, so the monomeric complex was experimentally observed. For dpo-, bpb-, and bpfb-bridged systems, all the negative ΔG values indicate that Borromean rings are the thermodynamically favored products. These calculated results are strongly supported by the experimentally observed Borromean-link structures. The calculations of ΔH and ΔG provide appropriate theoretical rationalization for the size-

dependent Borromean link structures, as well as theoretical support for further constructing interlocked species.

In summary, we developed a self-assembly method for constructing molecular Borromean rings. In the formation of molecular rectangles, through adjustment of their arm length, a series of size-dependent Borromean-link frameworks were synthesized. Not only the lengths of the short- and long-arm linkers, but also the ratio of long- to short-arm linker length play a key role in the formation of Borromean rings. The crystal structures and ESI-MS analysis of these complexes confirm the formation of Borromean-link frameworks both in solution and in the solid state. From DFT calculations, the ΔG values agree well with the experimental observations. The formation mechanism and requirements of molecular Borromean rings is proposed. These findings were even helpful to direct the self-assembly of other discrete interlocked species, which may facilitate the construction of molecular machines and nanoscale devices in the future.

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- [34] CCDC 966321 (**I-6**), 966322 (**I-7**), 966323 (**II-2**), 966324 (**II-3**), 966325 (**II-5**), 966326 (**I-2a**), 966327 (**I-4a**) and 966328 (**I-6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.