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Assembly and disassembly of a Zn_{10} high-nuclearity circular helicate†Zih-Syuan Wu,[‡] Jui-Ting Hsu,[‡] Chang-Chih Hsieh and Yih-Chern Horng*

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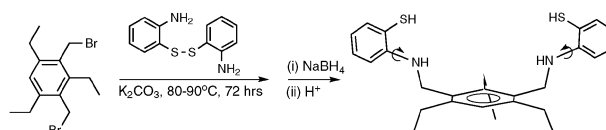
A nano-scale decanuclear Zn_{10} circular helicate is synthesized without the aid of counteranions during the assembly process, and can be totally disassembled into its reactants by specific anions.

The self-assembly of high-nuclearity coordination compounds, in particular, complexes exhibiting a helical array of ligand strands, has recently drawn much attention in the field of supramolecular chemistry.¹ However, the majority of these helicates have linear topologies with double- and triple-stranded arrangements—only a few examples of circular helical architectures have been reported.² Furthermore, the underlying principles governing the spontaneous formation of these circular helicates remain to be thoroughly elucidated. Factors reported to influence the formation of cyclic helicates include the size and coordination geometry of metal ions,³ structural features of the ligands,⁴ intramolecular (e.g. hydrogen bonding)⁵ and intermolecular (e.g. template effects of anions)⁶ interactions, and kinetic and thermodynamic controls.⁷ However, to construct a higher-nuclearity circular helicate, the effects of the net positive charge (NPC) of the circular helicate portion on its formation and the ease of isolation have to be considered. For instance, among cationic circular helicates with published structures composed of only divalent metal ions and neutral ligands, the maximum reported nuclearity is five with a high NPC of 10.^{8,9} The only two reported hexanuclear species were synthesized either by using monovalent metal ions (NPC: 6)¹⁰ or through the coordination of counteranions to the divalent metal centers (NPC: 0).¹¹ Thus far, the octonuclear circular helicate reported by Jones *et al.* represents the highest nuclearity for a cyclic helicate (NPC: 3) in the literature.¹² In this case, a monoanionic bis-bidentate ligand was used as a bridge between two adjacent Co^{2+} ions and a counteranion was encapsulated in the central cavity. It seems that the net charges of the ligand and assembled helicates play important roles in the construction of larger cyclic circular helicates. Although the strategy of ligand deprotonation through electrochemical synthesis was employed by Bermejo *et al.* to avoid the effects of counteranions in order to obtain cluster helicates,¹³ the use of a dithiolate bis-bidentate ligand to

construct a high-nuclearity circular helicate has not been reported before. In light of these observations, we designed and prepared a dianionic bis-bidentate ligand to coordinate divalent metal ions and successfully used it to obtain a neutral decanuclear circular helicate without any entrapped counteranions. In addition, total disassembly of the circular helicate by specific anions was achieved.

Recently, a 1,3-bis(methylene)phenylene spacer was employed in the pyridylimine ligand to facilitate the formation of trinuclear circular helicates with Ni^{2+} or Cu^{2+} ions.¹⁴ In the structures of these helicates, the ligands adopt the most extended conformation, with the two methylene groups pointing in opposite directions (up and down from the phenyl ring). We forced the two bidentate domains to orient toward the same side of the spacer by introducing three ethyl groups on the benzene ring of the spacer, since it is well known that the substituents attached to the 2,4,6-positions of 1,3,5-triethylbenzene turn to orient on the opposite side of the benzene plane relative to the ethyl groups.¹⁵ Furthermore, to minimize the positive charge associated with high-nuclearity polymer formation when the ligand reacts with divalent metal ions, we introduced a negative charge (thiolate) at each binding domain. The dithiol ligand (H_2L) was prepared in a manner similar to its trithiol analogue¹⁶ in 53% yield by the reaction of 2,4-bis(bromomethyl)-1,3,5-triethylbenzene with 2,2'-aminophenyl disulfide in CH_3CN followed by reduction and protonation (Fig. 1 and ESI†). This ligand has two bidentate chelating binding domains separated by a rigid 1,3-bis(methylene)phenylene spacer, which, together with the expected flexibility of the ligand (the free rotation of thiophenol around the N–C (phenyl) bond and the stereo-configuration around N), should prevent both aminothiophenolate units from chelating to the same metal ion, and hence facilitate the formation of high-nuclearity species.

With the knowledge that group 12 metals can form complexes with various thiolate ligands,¹⁷ we investigated the complexations of L^{2-} with Hg^{2+} , Cd^{2+} and Zn^{2+} ions. In a typical reaction, 1 equiv. of M^{2+} ($\text{M} = \text{Hg}, \text{Cd}$ or Zn) was added to a CH_3CN solution of 1 equiv. of H_2L and 2 equiv. of NEt_3 with stirring to afford a light-yellow complex as a precipitate in high yield (ESI†).

Fig. 1 Synthesis of H_2L .

Department of Chemistry, National Changhua University of Education, 1 Jin-De Road, Changhua 50058, Taiwan.

E-mail: ychorng@cc.ncue.edu.tw; Fax: +886 4721 1190

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‡ The authors contributed equally to this work.

The use of NaH instead of NEt_3 in this gave similar results. However, no reaction proceeded when the deprotonation step with NEt_3 was omitted. Elemental analysis results of the precipitates were consistent with the formula $(\text{ML})_n$. The ^1H NMR spectra of H_2L (in CDCl_3), Hg (in CDCl_3) and Cd (in DMSO-d_6) complexes showed only half a set of protons, indicating the chemical equivalence of the two binding domains within one ligand (ESI†). Interestingly, the Zn complex was found to have a complicated ^1H NMR spectrum. Through ^1H - ^1H COSY and ^1H - ^{13}C HSQC NMR experiments (ESI†), each signal in the ^1H NMR spectrum was assigned unambiguously. This showed that only one type of ligand conformation exists with two chemically non-equivalent binding sites. The chemical shifts of the two sets of aromatic protons on the binding strands were spread over 5.1 to 7.9 ppm, indicating significant shielding effects on several protons. This shielding effect was also observed in other polynuclear circular helicates.^{9,10}

Diffusion of pentane into a THF/1,4-dioxane (v/v 4 : 1) solution of the Hg complex at 4 °C afforded X-ray quality crystals,[§] the solid-state structure of which revealed neutral double-strand dinuclear mesocate Hg_2L_2 (ESI†). As expected, the two binding strands of each ligand were oriented at the same side of the spacer. Each of the Hg^{2+} centers coordinates to the aminothiophenolate S donors from two adjacent ligands with a straight linear coordination (Hg-S : 2.327(5), 2.329(5) Å; S-Hg-S = 177.4(2)°). A short $\text{Hg}^{2+} \cdots \text{O}$ contact interaction between Hg^{2+} and the O donor of 1,4-dioxane was also revealed in the structure ($\text{Hg} \cdots \text{O}$: 2.82(2) Å). Unfortunately, we were not able to obtain single crystals of the Cd complex suitable for X-ray diffraction studies. However, a dinuclear Cd complex is expected based on HRMS (ESI) analysis.

Recrystallization of the Zn compound from CHCl_3 by hexane diffusion at 4 °C afforded X-ray quality crystals,[§] the solid-state structure of which interestingly revealed a neutral decanuclear circular helicate $(\text{ZnL})_{10}$ (Fig. 2). This structure represents the highest-nuclearity circular helicate reported thus far. In the case of Zn(II), only pentanuclear circular helicates have been reported.⁹

Each Zn(II) center has a four-coordinate pseudo-tetrahedral coordination environment bound to two bidentate aminothiophenolate units from two different ligands. The dihedral angle between the ZnS_2 and ZnN_2 planes (62.8(1)–66.3(1)°) and the bond distances of the Zn-S (2.260(2)–2.277(2) Å) and Zn-N (2.081(5)–2.151(4) Å) for each metal center are very similar to the values reported for mono-nuclear Zn(II) complexes with an N_2S_2 coordination set.¹⁷ Due to the restricted orientation of the two binding domains of the ligand, the distances between adjacent Zn(II) ions (6.04–6.27 Å) are much shorter than those in the Zn pentanuclear circular helicates (over 9.0 Å) reported recently.⁹ The ten spacers are alternately located 'above and below' the plane formed by the ten metal ions. The two bidentate strands of each ligand, flipped differently, interact with two metal ions from inside and outside the decagon, respectively. The ten Zn(II) centers alternately have Λ - and Δ -configurations, resulting in an overall *meso*-helicate. There are no obvious intramolecular non-covalent interactions within the helicate and no template molecules, whether counteranions or solvents, were necessary to stabilize the architecture of this cyclic species. This spontaneous formation of the high-nuclearity

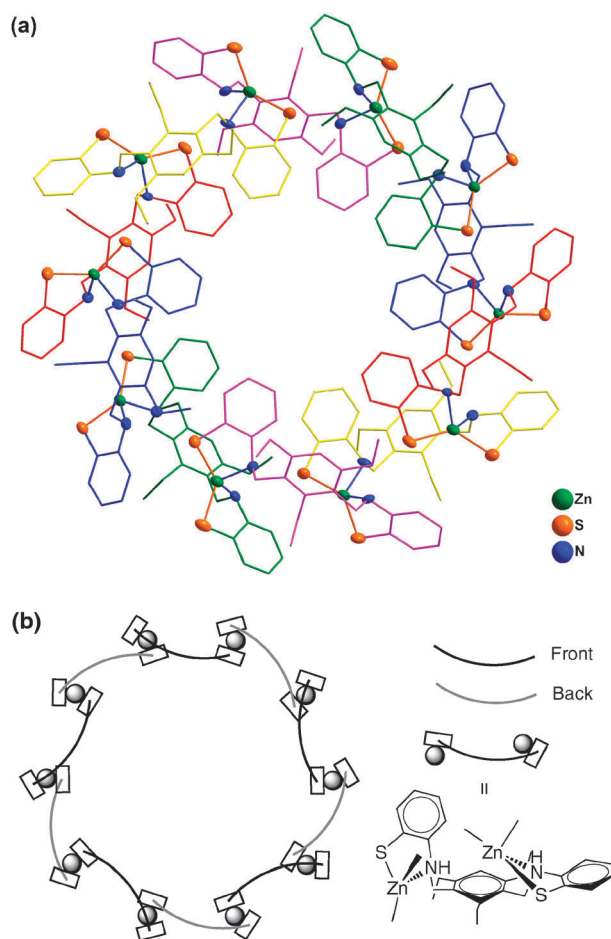


Fig. 2 (a) Crystal structure of $(\text{ZnL})_{10}$. The ligands in the same asymmetric unit are shown in the same color. Hydrogen atoms are omitted for clarity. (b) Schematic drawing of the decanuclear ring showing the helical ligand arrangement.

helicate is thus solely governed by the preferred binding geometry of the metal center, and the structural features and negative charges of the ligand. There is absolutely no need for counteranions to control the ring size by dictating the assembly pathway.

The space-filling representation of the decagonal helicate clearly indicates the nano-scale dimensions of the assembled structure. The outside diameter of the decagonal structure is about 2.9 nm with the thickness of the disc being about 1.2 nm, and the cavity has a diameter of ~0.86 nm. Moreover, the cyclic decameric $(\text{ZnL})_{10}$ units are packed together and stabilized by two types of $\text{CH} \cdots \pi$ interactions (totally eight for each unit). The molecular units stack in such a manner that channels of approximately oval cross section extending in the *b* direction are produced (ESI†).

Interestingly, we found that the neutral Zn(II) cyclic helicate can be totally disassembled by H_2PO_4^- ions. The reported monomeric Zn(II) complexes with similar N_2S_2 donor ligands were not luminescent in solution at RT.¹⁸ However, $(\text{ZnL})_{10}$ in CHCl_3 at RT exhibited a strong emission (at 530 nm) on irradiating with ultraviolet light (at 265 nm). When $(\text{ZnL})_{10}$ was titrated in CHCl_3 with various anions, including Cl^- , Br^- , I^- , ClO_4^- , PF_6^- , NO_3^- , HSO_4^- , no change occurred in the fluorescence intensity of $(\text{ZnL})_{10}$, although H_2PO_4^- showed

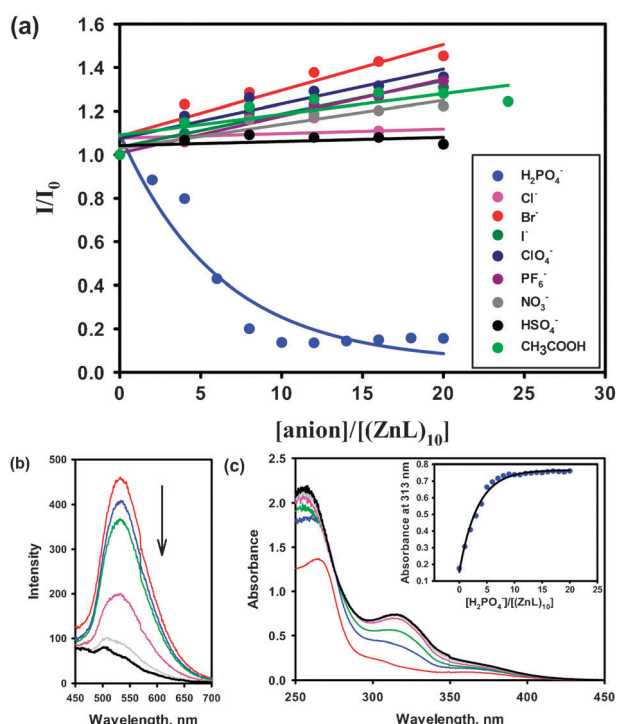


Fig. 3 (a) Plot of relative fluorescence intensity (I/I_0) of $[(\text{ZnL})_{10}]$ versus the mole ratio of anions added. Fluorescence (b) and absorption (c) titrations of $(\text{ZnL})_{10}$ with H_2PO_4^- . The black traces in (b) and (c) represent the spectra of H_2L at 0.10 mM. The starting concentration of $(\text{ZnL})_{10}$ for all titrations was 10 μM .

significant quenching (Fig. 3a and b). This quenching is not solely due to the protonation of the thiolates of the coordinated L^{2-} since even 20 equiv. of HSO_4^- and CH_3COOH acids have no effect on the fluorescence intensity of $(\text{ZnL})_{10}$. To better understand H_2PO_4^- binding, titrations using absorption spectroscopies were carried out between $(\text{ZnL})_{10}$ and different concentrations of H_2PO_4^- . Upon the addition of H_2PO_4^- , the initial absorbance band of $(\text{ZnL})_{10}$ was slightly shifted (from 300 to 313 nm) with increased intensity, and reached a saturation point after the addition of 10 equiv. (Fig. 3c). The absorption and ^1H NMR spectra of the final product showed characteristics nearly identical to that of the simple H_2L . These results indicate that H_2PO_4^- can induce total disassembly of the nano-scale cyclic helicate $(\text{ZnL})_{10}$ into its reactants H_2L and Zn^{2+} . To the best of our knowledge, this is the first example of total disassembly of synthetic circular helicates in the literature.

We realized the assembly of the remarkably high-nuclearity circular helicate $(\text{ZnL})_{10}$ through careful design of ligands, including structural features and charges. The procedure does not require the use of counteranions as templates for the spontaneous formation of these high-nuclearity metal based supramolecules. In addition, we observed selective fluorescent sensing of H_2PO_4^- anions by $(\text{ZnL})_{10}$ accompanied by total disassembly of the helicate.

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Notes and references

§ Crystal data for $\text{Hg}_2\text{L}_2 \cdot 1.5\text{C}_4\text{H}_8\text{O}_2$: $\text{C}_{52}\text{H}_{60}\text{Hg}_2\text{N}_4\text{S}_4 \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{C}_2\text{H}_4\text{O}$, $M = 1402.62$, monoclinic, $a = 9.9374(19)$ Å, $b = 26.392(4)$ Å, $c = 12.695(2)$ Å, $\alpha = 90.00^\circ$, $\beta = 108.149(6)^\circ$, $\gamma = 90.00^\circ$, $V = 3163.8(9)$ Å³, $T = 200(2)$ K, space group $P2_1/n$, $Z = 2$, $\mu(\text{MoK}\alpha) = 5.020$ mm⁻¹, 9084 reflections measured, 4795 independent reflections ($R_{\text{int}} = 0.0620$). The final R_1 values were 0.0751 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1810 ($I > 2\sigma(I)$). The final R_1 values were 0.1325 (all data). The final $wR(F^2)$ values were 0.2104 (all data). The goodness of fit on F^2 was 1.047. CCDC 856487; for $(\text{ZnL})_{10}$: $\text{C}_{260}\text{H}_{300}\text{N}_{20}\text{S}_{20}\text{Zn}_{10}$, $M = 5000.10$, monoclinic, $a = 26.7089(14)$ Å, $b = 25.6880(11)$ Å, $c = 27.0302(16)$ Å, $\alpha = 90.00^\circ$, $\beta = 117.334(7)^\circ$, $\gamma = 90.00^\circ$, $V = 16474.7(15)$ Å³, $T = 110(2)$ K, space group $P2_1/n$, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.884$ mm⁻¹, 80019 reflections measured, 38154 independent reflections ($R_{\text{int}} = 0.0809$). The final R_1 values were 0.0657 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1344 ($I > 2\sigma(I)$). The final R_1 values were 0.1730 (all data). The final $wR(F^2)$ values were 0.1414 (all data). The goodness of fit on F^2 was 0.965. CCDC 856488.

- (a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995;
- (b) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley and Sons, Chichester, 2000.
- (a) C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, *Coord. Chem. Rev.*, 2005, **249**, 705–726; (b) M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2004, **16**, 7–22; (c) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457–3498; (d) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005–2062.
- Y. Pang, S. Cui, B. Li, J. Zhang, Y. Wang and H. Zhang, *Inorg. Chem.*, 2008, **47**, 10317–10324.
- (a) E. C. Constable, C. E. Housecroft, T. Kulke, G. Baum and D. Fenske, *Chem. Commun.*, 1999, 195–196; (b) J. M. Senegas, S. Koeller, G. Bernardinelli and C. Piguet, *Chem. Commun.*, 2005, 2235–2237; (c) L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2002, **41**, 4244–4247.
- L. J. Childs, M. Pascu, A. J. Clarke, N. W. Alcock and M. J. Hannon, *Chem.–Eur. J.*, 2004, **10**, 4291–4300.
- (a) S. P. Argent, H. Adams, T. Riis-Johannessen, J. C. Jeffery, L. P. Harding, O. Mamula and M. D. Ward, *Inorg. Chem.*, 2006, **45**, 3905–3919; (b) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10956–10962.
- B. Hasenknopf, J.-M. Lehn, N. Boumediene, E. Leize and A. Van Dorsselaer, *Angew. Chem., Int. Ed.*, 1998, **37**, 3265–3268.
- (a) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1838–1840; (b) K. E. Allen, R. A. Faulkner, L. P. Harding, C. R. Rice, T. Riis-Johannessen, M. L. Voss and M. Whitehead, *Angew. Chem., Int. Ed.*, 2010, **49**, 6655–6658.
- (a) L. Bain, S. Bullock, L. Harding, T. Riis-Johannessen, G. Midgley, C. R. Rice and M. Whitehead, *Chem. Commun.*, 2010, **46**, 3496–3498; (b) O. R. Clegg, R. V. Fennessy, L. P. Harding, C. R. Rice, T. Riis-Johannessen and N. C. Fletcher, *Dalton Trans.*, 2011, **40**, 12381–12387.
- O. Mamula, A. von Zelewsky and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1998, **37**, 289–293.
- H. B. Tanh Jeazet, K. Gloe, T. Doert, O. N. Kataeva, A. Jager, G. Geipel, G. Bernhard, B. Buchner and K. Gloe, *Chem. Commun.*, 2010, **46**, 2373–2375.
- P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Chem. Commun.*, 1997, 1361–1362.
- M. R. Bermejo, A. M. González-Noya, R. M. Pedrido, M. J. Romero and M. Vázquez, *Angew. Chem., Int. Ed.*, 2005, **44**, 4182–4187.
- J. Hamblin, F. Tuna, S. Bunce, L. J. Childs, A. Jackson, W. Errington, N. W. Alcock, H. Nierengarten, A. Van Dorsselaer, E. Leize-Wagner and M. J. Hannon, *Chem.–Eur. J.*, 2007, **13**, 9286–9296.
- G. Hennrich and E. V. Anslyn, *Chem.–Eur. J.*, 2002, **8**, 2218–2224.
- Y.-C. Horng, T.-L. Lin, C.-Y. Tu, T.-J. Sung, C.-C. Hsieh, C.-H. Hu, H. M. Lee and T.-S. Kuo, *Eur. J. Org. Chem.*, 2009, 1511–1514.
- H. Fleischer, *Coord. Chem. Rev.*, 2005, **249**, 799–827.
- T. Kawamoto, M. Nishiwaki, Y. Tsunekawa, K. Nozaki and T. Konno, *Inorg. Chem.*, 2008, **47**, 3095–3104.