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Boronate Ester-Capped Helicates

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Abstract: Triple-stranded helicates were obtained by metal-templated multicomponent reactions of bispyridyloxime ligands with arylboronic acids. The helicates feature two hexa-coordinated M^{II} ions ($M = \text{Fe}, \text{Zn}, \text{or Mn}$), which are embedded in a macrobicyclic ligand framework, and two arylboronate ester capping groups. The latter can be used to introduce functional groups such as pyridines, aldehydes, nitriles, and carboxylic acids in apical position. The functionalized helicates have the potential to be used as nanoscale building blocks for more complex assemblies, as evidenced by the synthesis of a 3nm-sized trianglimine.

Linear and cyclic helicates have been studied extensively for more than 30 years.^[1–3] The first comprehensive review article was published by Piquet, Bernardinelli, and Hopfgartner in 1997.^[3] At that time, applications started to emerge. For example, helicates were used as selective hosts for cations or anions, or as starting materials for the synthesis of molecular knots.^[3] Since then, research on helicates has expanded and diversified considerably. Developments include the utilization of helicates as biomolecular probes,⁴ as catalysts,⁵ as molecular switches,^[3a,6] and as precursors for topologically complex molecular architectures.^[7] Moreover, some helicates were found to display spin-crossover behavior^[8] or act as single molecule magnets.^[9] Helicates have also been investigated in a biological and medicinal context, leading to the discovery of complexes with cytotoxic, antiviral or antibacterial properties.^[10]

The structural resemblance of double-stranded, linear helicates and duplex DNA has been noted repeatedly,^[1–3] with the discussion focusing on the helical arrangement of the ligands and the DNA strands, respectively. However, there is another similarity between duplex DNA and linear helicates: both tend to form rigid, rod-like structures.^[11] Duplex DNA has a width of around 2 nm and a persistence lengths of about 50 nm.^[12] When decorated with appropriate 'sticky ends', DNA rods can be employed to build highly elaborate molecular nanostructures.^[13] Linear helicates are much smaller than duplex DNA, but they still hold the potential to be used as nanoscale building blocks for more complex assemblies. A key challenge in this context is to synthesize helicates with 'sticky ends'.

In the following, we describe triple-stranded M_2L_3 -type helicates, which are capped by arylboronate ester groups. The aryl groups can be decorated with different functional groups, which could be used for the crosslinking of helicates via covalent or non-covalent bonds.

Our work was inspired by two classes of compounds: triple stranded, dinuclear helicates of type **A**, and boronate ester-capped pyridineoximate complexes of type **B** (Figure 1). The helicates can be prepared by M^{2+} -templated condensation reactions of bis-formylpyridine ligands with primary amines.^[14,15] Complexes of type **B** are obtained by M^{2+} -templated condensation reactions of phenylboronic acid with 2-acetylpyridineoxime.^[16] We hypothesized that it should be possible to merge the two synthetic approaches, allowing to access boronate ester-capped helicates of type **C**. The terminal arylboronate ester groups could then be used to introduce functional groups ('sticky ends') in a defined orientation, as it was shown for clathrochelatate complexes.^[17,18]

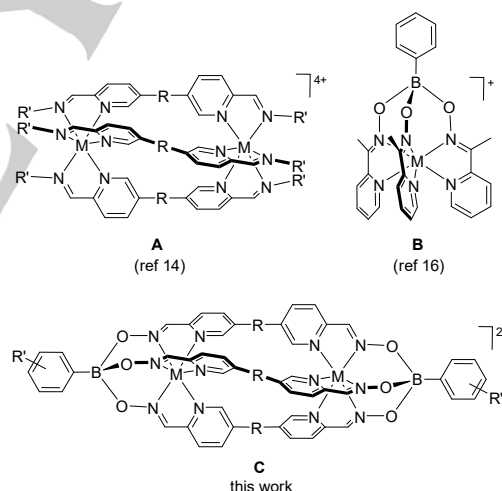


Figure 1. Triple-stranded helicates of type **A** (ref 14), boronate ester-capped pyridineoximate complexes of type **B** (ref 16), and the boronate ester-capped helicates **C** described in this work.

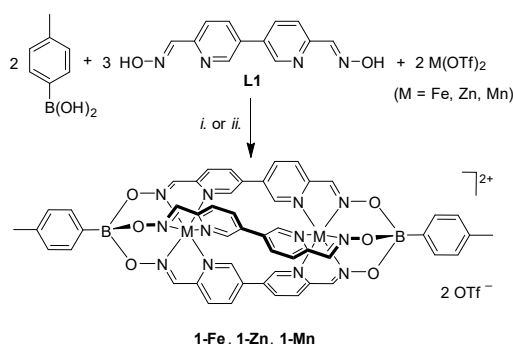
In order to test the feasibility of this approach, we first examined the reaction of *p*-tolylboronic acid (2 equiv), dioxime ligand **L1**^[19,20] (3 equiv), and $\text{Fe}(\text{OTf})_2$ (2 equiv) in acetonitrile. When the suspension was heated to 65 °C, we could observe slow dissolution of the starting materials and formation of a dark red solution. Analysis of the latter by mass spectrometry indicated the formation of the desired dinuclear complex **1-Fe**. Further studies showed that the reaction is more conveniently performed with microwave heating (100 °C, 90 min). Using this procedure, we were able to isolate complex **1-Fe** in 50% yield (Scheme 1).

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Attempts to prepare zinc(II) and manganese(II) complexes under similar conditions were not successful. However, using ethanol and a base instead of plain acetonitrile allowed preparation of **1-Zn** and **1-Mn** in yields of 52% and 50%, respectively (Scheme 1). Attempts to increase the yields by variation of the reaction conditions or the work-up procedure were unfortunately not successful.



Scheme 1. Synthesis of the helicates **1-Fe**, **1-Zn**, and **1-Mn**. Reagents and conditions: *i.*) M = Fe, CH₃CN, MW, 100 °C, 90 min; *ii.*) M = Zn or Mn, EtOH, NaHCO₃, MW, 100 °C, 90 min.

The complexes are moderately soluble in CH₃CN, CH₃OH, DMSO, DMF, or CH₃NO₂, but they display poor solubility in less polar solvents such as CH₂Cl₂ or CHCl₃. Analysis of solutions of **1-Fe** in CD₃CN by NMR spectroscopy showed well-resolved spectra, indicating that the Fe^{II} ions are in a low spin configuration. In contrast, the NMR data for **1-Mn** point to a paramagnetic complex. These findings are in line with what has been reported for mononuclear complexes of type **B**.^[16] Whereas **1-Zn** and **1-Mn** are not sensitive to oxygen, **1-Fe** needs to be handled under inert atmosphere.

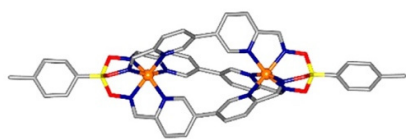
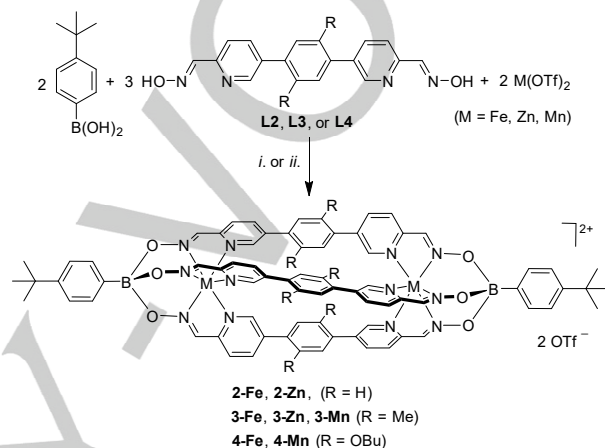


Figure 2. Molecular structure of helicate **1-Fe** in the crystal. Hydrogen atoms, solvent molecules, and anions (2 TfO⁻) are omitted for clarity. Color code: C, grey; N, blue; O, red; B, yellow; Fe, orange.

The molecular structure of **1-Fe** in the crystal was determined by single crystal X-ray diffraction (Figure 2). As expected, the two Fe^{II} ions are each coordinated to six nitrogen atoms (Fe-N_{av} = 1.95 Å). With an average twist angle^[21] of φ_{av} = 36°, the coordination geometry around the Fe centers is in-between that of a trigonal prism (φ = 0°) and that of an octahedron (φ = 60°). Iron complexes of type **B** show a similar geometry.^[16] The strong distortion from the usual octahedral geometry of Fe^{II} complexes is likely the result of the boronate ester capping group. It is worth noting that the combination of linear pyridylimine ligands with Fe^{II} salts tends to give tetrahedral assemblies with the general formula Fe₄L₆, and not dinuclear helicates.^[14b,22] We assume that the low twist angle of the Fe complex is a key factor in favoring a helicate structure in the case **1-Fe**.

Longer helicates can be obtained by using ligands **L2**, **L3** or **L4** with C₆H₂R₂ spacers between the pyridyloxime groups in combination with 4-*tert*-butylphenylboronic acid and M(OTf)₂ (M = Fe, Zn, or Mn) (Scheme 2). The corresponding complexes **2–4** were prepared in yields between 51% and 56% using similar reactions conditions as described for **1**, even though slightly longer reaction times were required for **4** (microwave heating for 4 h instead of 90 min). The presence of six methyl or butoxy side chains results in an increased solubility of the helicates **3** and **4**, when compared to the moderately soluble helicate **1** and the poorly soluble helicate **2**.



Scheme 2. Synthesis of the helicates **2–4** (M = Fe, Zn, Mn). Reagents and conditions: *i.*) M = Fe, CH₃CN, MW, 100 °C, 90 min; *ii.*) M = Zn or Mn, EtOH, NaHCO₃, MW, 100 °C, 90 min, for **4**: 4 h.

The molecular structure of **3-Fe** was analyzed by single-crystal X-ray diffraction (Figure 3). The insertion of the C₆H₂Me₂ spacers leads to an increase of the Fe^{II}···Fe distance from 7.7 Å in **1-Fe** to 11.9 Å in **3-Fe**. The coordination geometry around the Fe centers in **3-Fe** is similar as it was observed for **1-Fe** (φ_{av} = 38°).

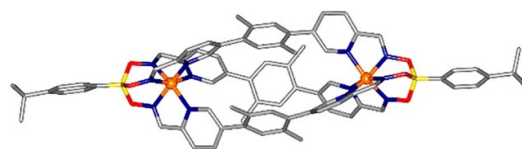


Figure 3. Molecular structure of helicate **3-Fe** in the crystal. Hydrogen atoms, solvent molecules, and anions (2 TfO⁻) are omitted for clarity. Color code: C, grey; N, blue; O, red; B, yellow; Fe, orange.

The redox properties of **3-Fe** were investigated by cyclic voltammetry. The measurements were performed in acetonitrile, using the Fc/Fc⁺ redox couple as external standard and TBAPF₆ as electrolyte. The data showed a reversible single electron process at $E_{1/2}$ = 1.08 V, which can be attributed to the oxidation of one metal center from Fe^{II} to Fe^{III} (for details, see Figure S126). A second oxidation could not be observed due to the limited window of the CD₃CN/TBAPF₆ system. CV measurements in DMF indicated a reduced stability of the helicate, and more detailed investigations were not performed.

Having established a protocol for the synthesis of boronate ester-capped helicates, we next examined if we could use the

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arylboronic acid to introduce functional groups. The potential danger of this approach is an interference of the functional group with the metal-templated condensation reactions (e.g. by coordination of the functional group to the metal ion). However, we found that such an interference is not an issue, and different functional groups could be introduced without compromising the yield.

First, we examined reactions of $\text{Fe}(\text{OTf})_2$ with 5-methoxypyridine-3-boronic acid using the bispyridyloxime ligands **L1** and **L3**. The resulting helicates **1-Fe-a** and **3-Fe-a** were isolated in 55% and 60% yield, respectively (Figure 4). Based on the crystallographic data for **1-Fe** and **3-Fe**, we estimate that the N-donor groups in **3-Fe-a** are approximately 2.1 nm (**1-Fe**) and 2.5 nm (**3-Fe**) apart from each other. The functionalized helicates **1-Fe-a** and **3-Fe-a** therefore represents nanoscale metallogligands,^[23] which might find applications in the synthesis of large metallocupramolecular structures.^[24] Building blocks with aldehyde functions are of interest for the construction of nanostructures using dynamic covalent imine chemistry.^[25] We have synthesized the helicates **1-Fe-b** and **3-Fe-b** using 4-formylphenylboronic acid. As in the other cases, the yields for these complexes are around 50%. Furthermore, we have synthesized helicates with cyano (**1-Fe-c** and **3-Fe-c**), bromo (**1-Fe-d** and **3-Fe-d**), and carboxylic acid functions (**1-Zn-e** and **3-Zn-e**) in *para* position using the corresponding arylboronic acids (Figure 4). These helicates represent potential metallogligands for coordination polymers and metal organic frameworks.

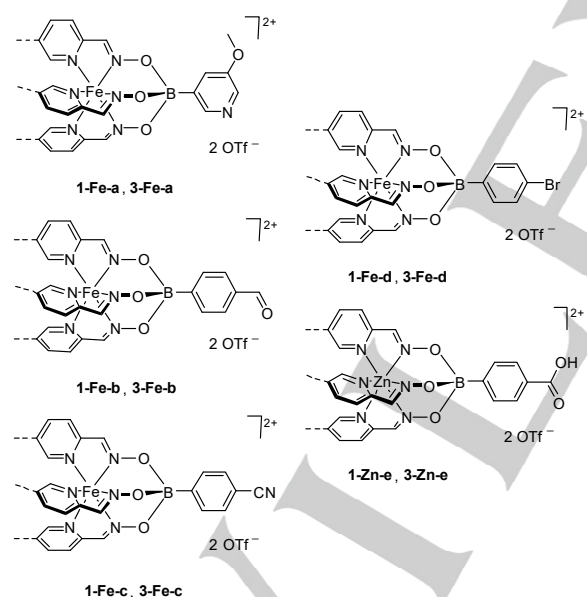
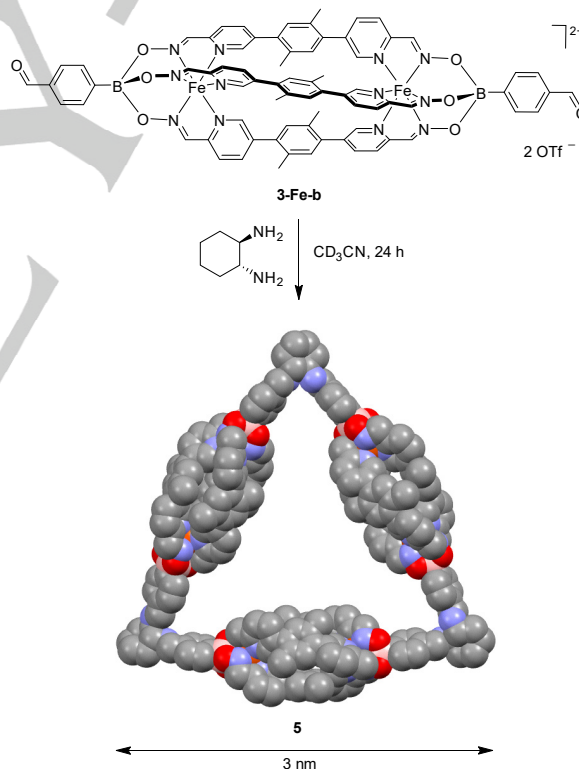


Figure 4. Helicates with functionalized arylboronate ester caps.

To demonstrate that boronate ester-capped helicates can be used as nanoscale building blocks, we have investigated the polycondensation reaction of dialdehyde **3-Fe-b** with (1*R*,2*R*)-1,2-diaminocyclohexane. This reaction was expected to give a 'trianglimine'^[26] via a [3+3] condensation. Trianglimines have been studied extensively over the last years, but significantly shorter dialdehydes are typically employed to build these macrocycles.^[26,27]

A common solvent for the formation of trianglimines is dichloromethane, but helicate **3-Fe-b** is poorly soluble in CH_2Cl_2 . Therefore, we focused on reactions in acetonitrile, in which both, the dialdehyde and the diamine, are well soluble. Using deuterated CD_3CN , we were able to follow the reaction by ^1H NMR spectroscopy. At room temperature, the disappearance of the aldehyde CHO signal at $\delta = 10.08$ ppm was observed within few hours ($[\text{dialdehyde}] = [\text{diamine}] = 5.4$ mM). After 24 hours, the NMR spectrum indicated that a defined new product had formed in high yield (> 95%), and the chemical shifts matched what is expected for a trianglimine. We are not able to comment on the diastereoselectivity of the macrocyclization. Since the starting materials (helicate and diamine) are both chiral, one can expect the formation of diastereoisomers. However, these isomers are not necessarily resolved by ^1H NMR spectroscopy. DOSY analysis showed that the new structure is larger than the helicate **3-Fe-b** ($D_t(\text{3-Fe-b}) = 7.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and $D_t(\text{5}) = 6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, see Figures S64 and S122). Additional evidence for the formation of a trianglimine was obtained by high resolution ESI mass spectrometry (for details, see Figure S123). Dominant peaks in the spectrum can be attributed to trianglimine **5** with a variable number of OTf^- anions: $[\text{5-OTf}]^{5+}$, $[\text{5-2OTf}]^{4+}$ and $[\text{5-3OTf}]^{3+}$.



Scheme 3. Synthesis of trianglimine **5**. The molecular structure of the macrocycle was obtained by molecular modelling using the Spartan software (H atoms are not shown).^[28] Color code: C, grey; N, violet; O, red; B, pink; Fe, orange.

To conclude: we have shown that boronate-ester capped helicates can be obtained by metal-templated multicomponent reactions of bispyridyloxime ligands with arylboronic acids. The polycondensation reactions are compatible with functionalized

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arylboronic acids. Consequently, it is possible to prepare helicates with different functional groups in apical position, such as pyridines, nitriles, aldehydes, and carboxylic acids. The functionalized helicates have the potential to be used as nanoscale building blocks for more complex assemblies. As a proof-of-concept, we have synthesized a trianglimine by condensation of a 4-formylphenylboronate ester-capped helicate with (1*R*,2*R*)-1,2-diaminocyclohexane. With a size of approximately 3 nm, the resulting macrocycle is the largest trianglimine reported to date.

Acknowledgements

We thank Dr. Aurélien Bornet and Cesare Berton for the help with the NMR measurements, Ophélie M. Planes for the help with CV measurements and Dr. Mathieu Marmier for fruitful discussions.

Keywords: helicate • supramolecular chemistry • dynamic covalent chemistry • condensation reaction • trianglimine

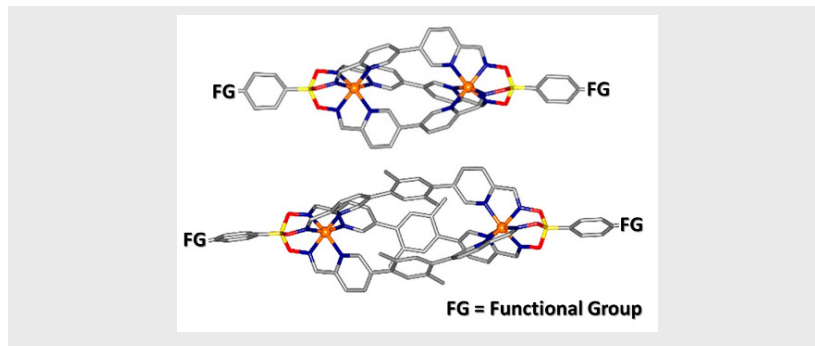
- [1] For a seminal publication about linear helicates, see: J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565–2569.
- [2] For seminal publications about circular helicates, see: a) B. Hasenknopf, J.-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.* **1997**, *119*, 10956–10962; b) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838–1840.
- [3] For reviews about helicates, see: a) M. Albrecht, X. Chen, D. Van Craen, *Chem. Eur. J.* **2019**, *25*, 4265–4273; b) A. P. Panneerselvam, S. S. Mishra, D. K. Chand, *Chem. Sci.* **2018**, *130*, 96–130; c) M. Boiocchi, L. Fabbrizzi, *Chem. Soc. Rev.* **2014**, *43*, 1835–1847; d) M. J. Hannon, L. Childs, *Supramol. Chem.* **2004**, *16*, 7–22; e) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; f) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062.
- [4] J.-C. G. Bünzli, *Chem. Rev.* **2010**, *110*, 2729–2755.
- [5] a) R. Arunachalam, E. Chinnaraja, A. Valkonen, K. Rissanen, S. K. Sen, R. Natarajan, P. S. Subramanian, *Inorg. Chem.* **2018**, *57*, 11414–11421; b) E. Chinnaraja, R. Arunachalam, K. Samanta, R. Natarajan, P. S. Subramanian, *Adv. Synth. Catal.* **2020**, *362*, 1–13.
- [6] a) A. C. N. Kwamen, G. S. de Macedo, C. Wiederhold, I. M. Oppel, M. Albrecht, *Chem. Eur. J.* **2020**, *26*, 3829–3833; b) X. Chen, T. M. Gerger, C. Räuber, G. Raabe, C. BGöb, I. M. Oppel, M. Albrecht, *Angew. Chem. Int. Ed.* **2018**, *57*, 11817–11820; c) Y. Suzuki, T. Nakamura, H. Iida, N. Ousaka, E. Yashima, *J. Am. Chem. Soc.* **2016**, *138*, 4852–4859; d) K. Miwa, Y. Furusho, E. Yashima, *Nature Chem.* **2010**, *2*, 444–449.
- [7] S. D. P. Fielden, D. A. Leigh, S. L. Woltering *Angew. Chem. Int. Ed.* **2017**, *56*, 11164–11194.
- [8] A. J. McConnell, *Supramol. Chem.* **2018**, *30*, 858–868.
- [9] For selected examples, see: a) R. Diego, A. Pavlov, M. Darawsheh, D. Aleshin, J. Nehrkorn, Y. Nelyubina, O. Roubeau, V. Novikov, G. Aromi, *Inorg. Chem.* **2019**, *58*, 15, 9562–9566; b) A. K. Mondal, H. S. Jena, A. Malviya, S. Konar, *Inorg. Chem.* **2016**, *55*, 5237–5244; c) H. Li, P. Chen, W. Sun, L. Zhang, P. Yan, *Dalton Trans.* **2016**, *45*, 3175–3181; d) S.-Y. Lin, L. Zhao, Y.-N. Guo, P. Zhang, Y. Guo, J. Tang, *Inorg. Chem.* **2012**, *51*, 10522–10528.
- [10] For selected examples, see: a) S. J. Allison, D. Cooke, F. S. Davidson, P. I. P. Elliott, R. A. Faulkner, H. B. S. Griffiths, O. J. Harper, O. Hussain, P. J. Owen-Lynch, R. M. Phillips, C. R. Rice, S. L. Shepherd, R. T. Wheelhouse, *Angew. Chem. Int. Ed.* **2018**, *57*, 979–9804; b) L. Cardo, I. Nawroth, P. J. Cail, J. A. McKeating, M. J. Hannon, *Scientific Reports* **2018**, *8*, 13342; c) V. Brabec, S. E. Howson, R. A. Kaner, R. M. Lord, J. Malina, R. M. Phillips, Q. M. A. Abdallah, P. C. McGowan, A. Rodger, P. Scott, *Chem. Sci.* **2013**, *4*, 4407–4416; d) S. E. Howson, A. Bolhuis, V. Brabec, G. J. Clarkson, J. Malina, A. Rodger, P. Scott, *Nature Chem.* **2012**, *4*, 31–36; e) G. I. Pascu, A. C. G. Hotze, C. Sanchez-Cano, B. M. Kariuki, M. J. Hannon, *Angew. Chem. Int. Ed.* **2007**, *46*, 4374–4378.
- [11] There are examples of helicates with a high degree of conformational freedom, e.g. the ‘flexicate’ assemblies described by Scott and co-workers (ref. 10d).
- [12] The flexibility of dsDNA depends to the lengths of the strands and on the conditions. For a discussion, see: A. Garai, S. Saurabh, Y. Lansac, P. K. Maiti, *J. Phys. Chem. B* **2015**, *119*, 11146–11156.
- [13] N. C. Seeman, H. F. Sleiman, *Nature Rev. Mater.* **2017**, *3*, 1–23.
- [14] a) B. Sun, S. S. Nurtilla, J. N. H. Reek, *Chem. Eur. J.* **2018**, *24*, 14693–14700; b) N. Ousaka, S. Grunder, A. M. Castilla, A. C. Whalley, J. F. Stoddart, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 15528–15537.
- [15] The inverse condensation chemistry (diamine plus formylpyridine) is more commonly employed for the synthesis of helicates. For selected examples, see refs. 10b–e and: a) T. F. Miller, L. R. Holloway, P. P. Nye, Y. Lyon, G. J. O. Beran, W. H. Harman, R. R. Julian, R. J. Hooley, *Inorg. Chem.* **2018**, *57*, 13386–13396; b) E. Fazio, C. J. E. Haynes, G. De la Torre, J. R. Nitschke, T. Torres, *Chem. Commun.* **2018**, *54*, 2651–2654; c) L. R. Holloway, M. C. Young, G. J. O. Beran, R. J. Hooley, *Chem. Sci.* **2015**, *6*, 4801–4806; d) M. J. Hannon, C. L. Painting, N. W. Alcock, *Chem. Commun.* **1999**, 2023–2024.
- [16] A. A. Pavlov, S. A. Savkina, A. S. Belov, Y. V. Nelyubina, N. N. Efimov, Y. Z. Voloshin, V. V. Novikov, *Inorg. Chem.* **2017**, *56*, 6943–951.
- [17] a) S. M. Jansze, K. Severin *K. Acc. Chem. Res.* **2018**, *51*, 2139–2147; b) Y. Voloshin, I. Belaya, R. Kramer, *Cage Metal Complexes; Clathrochelates Revisited*; Springer International Publishing: New York, **2017**; c) M. D. Wise, K. Severin, *Chimia* **2015**, *69*, 191–195.
- [18] For selected example of arylboronate ester-capped clathrochelate complexes with functional groups in apical position, see: a) G. E. Zelinskii, A. S. Belov, A. V. Vologzhanina, I. P. Limarev, P. V. Dorovatovskii, Y. V. Zubavichus, E. G. Lebed, Y. Z. Voloshin, A. G. Dedov, *Polyhedron* **2019**, *160*, 108–114; b) S. M. Jansze, G. Cecot, M. D. Wise, K. O. Zhurov, T. K. Ronson, A. M. Castilla, A. Finelli, P. Pattison, E. Solari, R. Scopelliti, G. E. Zelinskii, A. V. Vologzhanina, Y. Z. Voloshin, J. R. Nitschke, K. Severin, *J. Am. Chem. Soc.* **2016**, *138*, 2046–2054; c) G. E. Zelinskii, S. D. Dudkin, A. S. Chuprin, A. A. Palov, A. V. Vologzhanina, E. G. Lebed, Y. V. Zubavichus, Yan Z. Voloshin, *Inorg. Chim. Acta* **2017**, *463*, 29–35; d) M. D. Wise, J. J. Holstein, P. Pattison, C. Besnard, E. Solari, R. Scopelliti, G. Bricogne, K. Severin, *Chem. Sci.* **2015**, *6*, 1004–1010; e) E. G. Lebed, A. S. Belov, A. V. Dolganov, A. V. Vologzhanina, V. V. Novikov, E. V. Kuznetsov, Y. Z. Voloshin, *Inorg. Chem. Commun.* **2013**, *33*, 57–62; f) M. D. Wise, A. Ruggi, M. Pascu, R. Scopelliti, K. Severin, *Chem. Sci.* **2013**, *4*, 1658–1662.
- [19] B. S. Pilgrim, D. A. Roberts, T. Lohr, T. K. Ronson, J. R. Nitschke, *Nature Chem.* **2017**, *9*, 1276–1281.
- [20] X. Zhang, J. Liu, J. Zhang, J. Huang, C. Wan, C. Li, X. You, *Polyhedron* **2013**, *60*, 85–92.
- [21] J. Zhang, J. Li, L. Yang, C. Yuan, Y. Zhang, Y. Song, *Inorg. Chem.* **2018**, *57*, 3903–3912.
- [22] D. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* **2018**, *51*, 2423–2436.
- [23] a) F. Li, L. F. Lindoy, *Aust. J. Chem.* **72**, 731–741; b) S. Srivastava, R. Gupta, *CrystEngComm* **2016**, *18*, 9185–9208; c) G. Kumar, R. Gupta, *Chem. Soc. Rev.* **2013**, *42*, 9403–9453.
- [24] For examples of the utilization of nanoscale polypyridyl ligands in metallosupramolecular chemistry, see: a) Y.-J. Hou, K. Wu, Z.-W. Wei, K. Li, Y.-L. Lu, C.-Y. Zhu, J.-S. Wang, M. Pan, J.-J. Jiang, G.-Q. Li, C.-Y. Su, *J. Am. Chem. Soc.* **2018**, *140*, 18183–18191; b) S. M. Jansze, D. Ortiz, F. Fadaei Tirani, R. Scopelliti, L. Menin, K. Severin, *Chem. Commun.* **2018**, *54*, 9529–9532; c) N. Singh, J. Singh, D. Kim, D. H. Kim, E.-H. Kim, M. S. Lah, K.-W. Chi, *Inorg. Chem.* **2018**, *57*, 3521–3528; d) A. A. Adeyemo, P. S. Mukherjee, *Beilstein J. Org. Chem.* **2018**, *14*, 2242–2249; e) G. Cecot, M. Marmier, S. Geremia, R. De Zorzi, A. V. Vologzhanina, P. Pattison, E. Solari, F. Fadaei Tirani, *J. Am. Chem. Soc.* **2017**, *139*, 8371–8381; f) J. Yang, M. Bhadbhade, W. A. Donald, H. Iranmanesh, E. G. Moore, H. Yan, J. E. Beves, *Chem. Commun.* **2015**, *51*, 4465–4468; g) A. Ardavan, A. M. Bowen, A. Fernandez, A. J. Fielding,

COMMUNICATION

- D. Kaminski, F. Moro, C. A. Muryn, M. D. Wise, A. Ruggi, E. J. L. McInnes, K. Severin, K.; G. A. Timco, C. R. Timmel, F. Tuna, G. F. S. Whitehead, R. E. P. Winpenny, *npj Quantum Inf.* **2015**, *1*, 15012.
- [25] a) J. F. Reuther, S. D. Dahlhauser, E. V. Anslyn, *Angew. Chem. Int. Ed.* **2019**, *58*, 74–85; b) K. Acharyya, P. S. Mukherjee, *Angew. Chem. Int. Ed.* **2019**, *58*, 8640–8653; c) Y. Jin, C. Yu, R. J. Denman, W. Zhang, *Chem. Soc. Rev.* **2013**, *42*, 6634–6654.
- [26] For a review, see: M. Kwit, J. Grajewski, P. Skowronek, M. Zgorzelak, J. Gawroński, *Chem. Rec.* **2019**, *19*, 213–237.
- [27] For selected examples, see: a) N. Prusinowska, M. Bardiński, A. Janiak, P. Skowronek, M. Kwit, *Chem. Asian J.* **2018**, *13*, 2691–2699; b) Z. Wang, H. F. Nour, L. M. Roch, M. Guo, W. Li, K. K. Baldrige, A. C.-H. Sue, M. A. Olson, *J. Org. Chem.* **2017**, *82*, 2472–2480; c) J. Gajewy, J. Szymkowiak, M. Kwit, *RSC Adv.* **2016**, *6*, 53358–53369; d) H. F. N. Nour, M. F. Matej, B. S. Bassil, U. Kortz, N. Kuhnert, *Org. Biomol. Chem.*, **2011**, *9*, 3258–3271; e) J. Hodačová, M. Buděšínský, *Org. Lett.* **2007**, *9*, 5641–5643; f) M. Kwit, P. Skowronek, H. Kolbon, J. Gawroński, *Chirality* **2005**, *17*, S93–S100; g) N. Kuhnert, G. M. Rossignolo, A. Lopez-Periago, *Org. Biomol. Chem.* **2003**, *1*, 1157–1170; h) J. Gawroński, H. Kolbon, M. Kwit, A. Katrusiak, *J. Org. Chem.* **2000**, *65*, 5768–5773.
- [28] Wavefunction 2018, Spartan'18 (Wavefunction, Inc.).

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Boronate Ester-Capped Helicates

Helicates with caps: metal-templated multicomponent reactions of bispyridyloxime ligands with arylboronic acids give helicates with terminal arylboronate ester groups. The latter can be used to introduce functional groups such as pyridines, aldehydes, nitriles, and carboxylic acids in apical position.