

# ChemComm

Accepted Manuscript



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 [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) 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.

## COMMUNICATION

## Oligoamylose-Entwined Porphyrin: Excited-State Induced-Fit for Chirality Induction

Cite this: DOI: 10.1039/x0xx00000x

Mitsuhiko Morisue,<sup>\*a</sup> Takashi Yumura,<sup>b</sup> Risa Sawada,<sup>c</sup> Masanobu Naito,<sup>d</sup> Yasuhisa Kuroda<sup>a</sup> and Yoshiki Chujo<sup>c</sup>Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

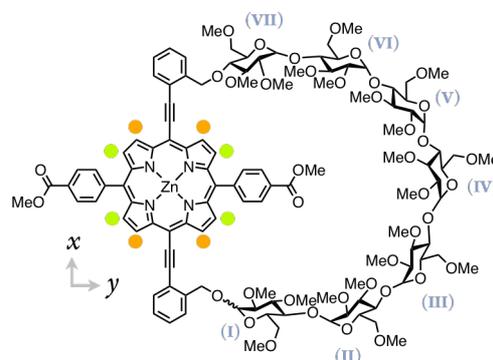
**An oligoamylose-strapped porphyrin displayed circularly polarized luminescence (CPL) in the  $S_1$  state despite it being silent in circularly dichroism (CD) in the ground state, suggesting chirality induction in the photoexcited porphyrin moiety from the oligoamylose-strap in the photoexcited state.**

Chromophores that show circularly polarized luminescence (CPL) are an attractive class of optical materials.<sup>1</sup> CPL originates from chiral dispersive interaction in the photoexcited state, as approximated by the quotient of the electronic dipole moment divided by the magnetic dipole moment.<sup>2</sup> Therefore, CPL is an alternative application of electromagnetic properties of light in Maxwell's equation. A photoexcited chiral chromophore can generate CPL even when no chiroptical properties are observed in the ground state.<sup>3</sup> However, organic chromophores that exhibit large differential luminescence of left- or right-handed CPL have been primarily limited to chiral chromophore aggregates.<sup>1a-c</sup> Otherwise, the structurally rigid  $\pi$ -framework including helicenes,<sup>4</sup> biaryls,<sup>5</sup> and sophisticatedly designed molecules,<sup>6</sup> has been indispensable to suppress racemisation both in the ground state and the excited state. In this context, exploration of non-aggregated and non-polymeric CPL-active chromophore is a significant challenge.<sup>1d,7</sup> Given that there is a trade-off between the electronic dipole moment and the magnetic dipole moment, conformational change of a chromophore in the photoexcited state could be a potential strategy to impart chiral nature to the photophysical properties of the chromophore.

Contrasting with the conventional approaches, we investigated whether an induced-fit system<sup>8</sup> could be adaptable to induce chirality in an intrinsically achiral chromophore in the photoexcited state in a chiral environment. In this context, a spiral channel of a chiral biological entity may be appropriate to transfer chirality to the intrinsically achiral chromophore. This report describes a comprehensive proof-of-concept study to tackle challenges in developing a new class of CPL materials.

A spiral channel can be created by length-mismatched clamping between each terminal of a rigid rotatable axle, which leads to the axle moiety self-encapsulating in the channel. For example, clipping the side-groups of the oligomeric  $\pi$ -systems has been explored to provide helical  $\pi$ -systems, which has been coined as "geländer oligomer" by Vögtle and coworkers.<sup>9</sup> Gladysz and coworkers also reported a similar strategy to form spiral structures by entwining a stiff axle.<sup>10</sup> Such a vine-twining analogy is also intriguing to tune the electronic properties by twisting the axle of the chromophore.<sup>11</sup> Here we present a biological entity as a chiral adaptable channel that includes an achiral chromophore.

Amylose is a polysaccharide composed of a D-glucose backbone connected via  $\alpha(1\rightarrow4)$ -glycoside linkages, adopting a 6<sub>1</sub> left-handed helix (6 glucopyranose units in one turn).<sup>12</sup> This is of particular interest because the formation of the amylose-iodine inclusion complex, which is known as a "starch blue reaction", is one of the most representative examples of an induced-fit host-guest binding of a helical polymer.<sup>13</sup> The interior channel of the folded amylose encapsulates versatile lipophilic guest molecules, such as chromophores and polymers.<sup>14,15</sup> The most representative examples



**Scheme 1.** Chemical structure of oligoamylose-strapped porphyrin **1**.

are cyclic analogues of oligoamylose (cyclodextrins), which have been a key element in host-guest chemistry,<sup>16</sup> and some of which can exhibit CPL.<sup>17</sup>

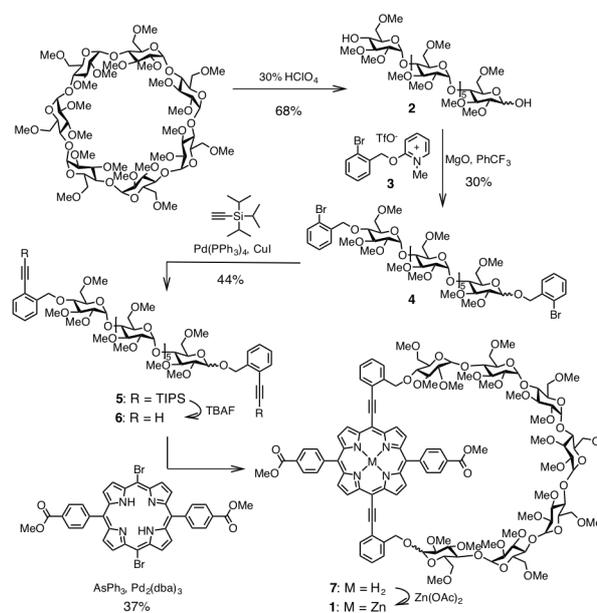
Herein, we design an oligoamylose-strapped porphyrin **1** (Scheme 1), with which an achiral porphyrin axle is self-folded by a helically twisted polysaccharide. A flexible oligoamylose-strap (per-*O*-methylated maltoheptaose) was tethered to the rigid porphyrin, wherein an interaction between the oligoamylose and porphyrin moiety occurred based on the fact that cyclodextrin derivatives were able to form exceptionally stable inclusion complexes with aqueous porphyrinoid.<sup>18,19</sup> With the aim of creating an induced-fit system through intramolecular host-guest interactions, the rotatable ethynylene linkages may be effective in inducing helicity around the porphyrin plane. Moreover, achiral porphyrin macrocycle is a privileged substrate to induce chirality.<sup>20</sup> At the same time, such macrocyclic cavity composed of porphyrin-cyclodextrin hybrid is also intriguing as a novel structural unit, the so-called "element-block",<sup>21</sup> in host-guest systems.<sup>22</sup>

The synthetic route is outlined in Scheme 2. Single scission of the glycoside linkage opened the ring of per-*O*-methylated  $\beta$ -cyclodextrin,<sup>23</sup> and both the 1<sup>(O)</sup>-hemiacetal and 4<sup>(VII)</sup>-hydroxy terminal of the methylated maltoheptaose **2** was simultaneously subjected to the Dudley's benzyl-transfer protocol<sup>24</sup> with **3**, and **4** was obtained in 30% yield. Each bromine-terminal of **4** was then introduced silylated acetylene by the Sonogashira-Hagihara coupling reaction to give **5**, which was then desilylated. The linear oligoamylose **6** was re-cyclized with the corresponding porphyrin. The oligoamylose-strapped porphyrin **7** was metallated with zinc ion. The products were satisfactory to identification by NMR and MALDI-TOF MS spectra, as described in the Supporting Information.<sup>25</sup>

Self-folded conformations were rationally simulated by the computational energy-minimized model study (B97D). In the *folded* conformation of **1** (Figure 1A), the distance between the ring-membered-oxygen atom of the glucose-(III) and the zinc atom is 2.3 Å, suggesting the existence of a coordination bond. The existence of multiple CH- $\pi$  interactions between the glucose and porphyrin plane were also predicted. The *folded* conformation gave rise to structural strain of the oligoamylose-strap, leading to a "chair"-to-"boat" conformational change of the glucose-(III) ring.

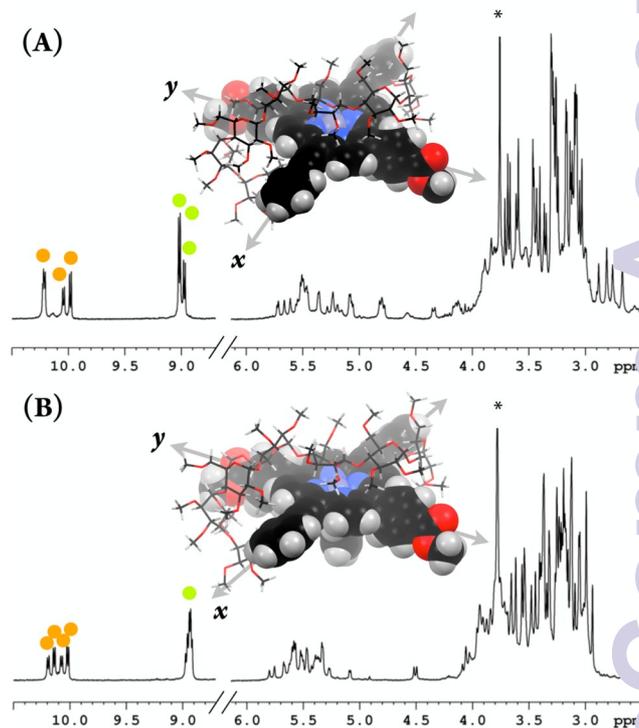
The *folded* conformation of **1** was verified by NMR spectroscopy in toluene-*d*<sub>6</sub>. The aromatic resonances of the porphyrin ring were heterogeneously multiplied due to the asymmetric environment of the oligoamylose strap (Figure 1A). Similarly, some of the methyl protons of oligoamylose-strap shifted upfield due to shielding in the vicinity of the porphyrin moiety. The computational structure was also supported by unambiguous nuclear Overhauser effect (NOE) correlations between the protons of the oligoamylose-strap and the aromatic resonances of porphyrin- $\beta$  and *meso*-aryl groups (Figure S1).<sup>25</sup> Therefore, **1** formed a self-inclusion complex at ambient temperature in toluene.

The addition of pyridine-*d*<sub>5</sub> as a competitively coordinating axial ligand ( $K_a = 2.6 \times 10^4 \text{ M}^{-1}$ ) disturbed the glucose-to-zinc axial coordination (Figure 1B). Then, **1**-Py showed no substantial NOE correlation between the aromatic resonances of porphyrin ring and the oligoamylose strap, unlike the results observed in toluene-*d*<sub>6</sub>. The glucose C1-protons (5.2–4.0 ppm) mostly shifted downfield upon

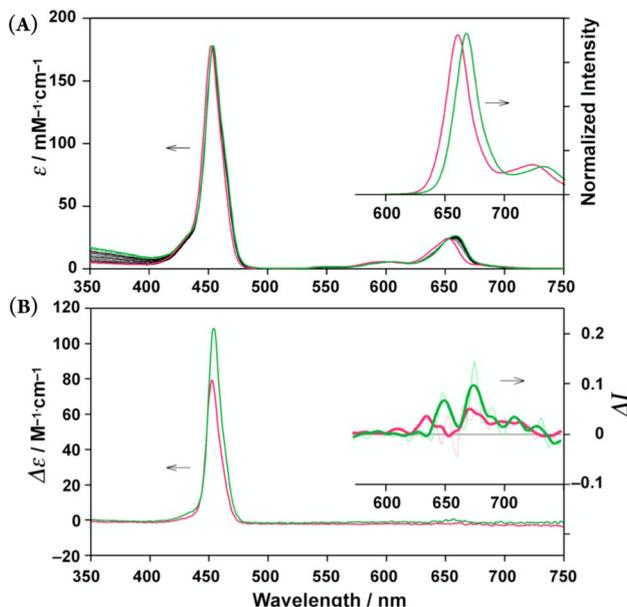


**Scheme 2.** Synthetic route of oligoamylose-strapped porphyrin **1**.

addition of pyridine-*d*<sub>5</sub>, suggesting that the protons of the oligoamylose strap were less shielded by the porphyrin ring (Figure 1B). At the same time, the methyl protons at 3.0–2.5 ppm shifted downfield. These results suggest that the folded conformation of **1** was disturbed in the presence of pyridine. Nevertheless, the oligoamylose-strap remained helical conformation. Actually, the



**Figure 1.** <sup>1</sup>H NMR spectra and computer-optimized structures of *folded* **1** in toluene-*d*<sub>6</sub> (A) and *semifolded* **1**-Py in the presence of 5% of pyridine-*d*<sub>5</sub> (B) at 298 K. Orange and green circles indicate the  $\beta$  protons as indicated in Scheme 1.



**Figure 2.** (A) Absorption spectra of **1** ( $1 \times 10^{-6}$  M) in the course of addition of pyridine (up to 3,750 equiv; red to green) in toluene at 298 °C. Inset shows normalized fluorescence spectra ( $\lambda_{\text{ex}} = 450$  nm). (B) CD spectra of *folded 1* (red) and *semifolded 1*-Py (green) in toluene. Inset shows CPL spectra ( $\lambda_{\text{ex}} = 450$  nm) with fitted curves (thick line).

protons at 10.3–9.9 ppm indicated an increase in dissymmetrisation along  $x$  direction following the addition of pyridine. The optimized structure suggested that the porphyrin moiety remained in the self-included structure even after pyridine bound the axial position. These experiments prove there are intramolecular interactions between the oligoamylose-strap and the porphyrin moiety. It is known that dipole interactions play a crucial role in the host–guest interaction of the polar cavity of cyclodextrin<sup>26</sup> in aqueous media<sup>18a,27</sup> and in nonpolar solvents.<sup>28</sup> Eventually, in the presence of pyridine, **1** adopted the *semifolded* conformation.

The chiroptical properties of **1** in the ground state were verified by circular dichroism (CD) (Figure 2B). An intense positive sign of induced CD (ICD) emerged at the Soret band ( $S_2$  state at 452 nm) of the achiral porphyrin moiety. It is known that glucose alone is not sufficient to induce a CD signal on the Soret band.<sup>29</sup> Instead, assuming that **1** was amenable to the ICD rule for an encapsulated molecule in a cyclodextrin cavity,<sup>30</sup> the positive CD signal suggested that the orientation of the porphyrin moiety was laid along the axis of the helical channel of the oligoamylose-strap, where the Soret transition along the  $y$  direction is predominant in electronic transition based on the time-dependent (TD)-DFT calculation.<sup>25,31</sup> The helically twisted conformation of the *meso*-aryl groups along the  $y$  direction may contribute to chiroptical properties to some extent. The absorption dissymmetry factor,  $g_{\text{abs}} = \Delta\epsilon/\epsilon = 2(\epsilon_{\text{left}} - \epsilon_{\text{right}})/(\epsilon_{\text{left}} + \epsilon_{\text{right}})$ , was  $+4.5 \times 10^{-4}$  at 452 nm for *folded 1* and  $+6.0 \times 10^{-4}$  at 454 nm for *semifolded 1*-Py. In contrast, the CD signal was only faint at the Q band ( $S_1$  state approximately 650 nm;  $g_{\text{abs}} < \sim 10^{-5}$  for **1** and **1**-Py). In these cases, the  $Q_x$  transition is predominantly based on the TD-DFT calculation.<sup>25,32</sup> Such diagonal orientations of the  $Q_x$  transition dipole

**Table 1.** Photophysical properties of  $S_1$  state of **1** upon excitation at 450 nm.

	$\lambda_{\text{max}}/\text{nm}(\Phi)^a$	$\tau/\text{ns}(\alpha)^b$	$g_{\text{lum}}^c$
<b>1</b>	659 (0.12)	0.51 (19%), 1.98 (81%)	$+2 \times 10^{-4}$ (664 nm)
<b>1</b> -Py	666 (0.13)	0.44 (21%), 1.68 (79%)	$+4 \times 10^{-4}$ (674 nm)

a) Emission maxima ( $\lambda_{\text{max}}$ ) and absolute quantum yield ( $\Phi$ ). b) Fluorescence lifetime ( $\tau$ ) and the normalized amplitude ( $\alpha$ ) determined from the fluorescence decay profiles. c) Luminescence anisotropy factor,  $g_{\text{lum}} = \Delta I/I = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$ .

could account for the contrasting chiroptical properties of the Q band in the CD spectra.

The porphyrin **1** showed fluorescence with absolute quantum yield ( $\Phi$ ) = 0.12 and 0.13 in the absence and presence of pyridine, respectively (Table 1). Upon excitation of the Soret band (450 nm), fluorescence was obtained from the Q band through internal conversion. The time-resolved fluorescence spectroscopy exhibited biexponential decay components regardless of the absence or presence of pyridine, suggesting structural relaxation in the excited state,<sup>25</sup> *i.e.*, induced-fit conformational change in the photoexcited state. Considering the fact that the photoexcited porphyrin plane is ruffled,<sup>33</sup> the porphyrin plane could be reorganized into a helical fashion at the photoexcited state. Moreover, it was recently reported that the vibrational mode is coupled with the photoexcited  $Q_y$  transition.<sup>30</sup> Together with the above TD-DFT results, we hypothesize that the electronic transition anisotropy is diagonally reorganized from the  $Q_x$  to  $Q_y$  transition at the photoexcited state. Under these conditions, **1** could display CPL.

Indeed, the emission from the  $S_1$  state of **1** was circularly polarized (Figure 2B). The luminescence with anisotropy factor,  $g_{\text{lum}}$  of  $+2 \times 10^{-4}$  at 664 nm and  $+4 \times 10^{-4}$  at 674 nm was observed for *folded 1* and *semifolded 1*-Py, respectively. These values remained the similar magnitudes of the  $g_{\text{abs}}$  values at the Soret band. These results are in sharp contrast to the Q band that is substantially silent in the CD spectra in the ground state. From these results, we conclude that the conformational change caused by photoexcitation induced chirality in the intrinsically achiral  $S_1$  state of porphyrin moiety of **1**. Moreover, the somewhat enhanced  $g_{\text{lum}}$  value resulting from the addition of pyridine suggests that the more adaptable the induced-fit system the more effective the induction of chirality.

In conclusion, we demonstrated chirality induction based on the excited state induced-fit mechanism. A spiral channel created by a flexible oligoamylose-strap definitely had a chiral impact on the photoexcited conformational change of the achiral porphyrin axle to exhibit explicit CPL, although the  $g_{\text{lum}}$  magnitude of **1** was still ranged at a moderate level for a non-aggregated chromophore. Excited-state induced-fit mechanisms for chirality induction have highlighted a new potential approach to develop CPL-active chromophores. Further study of host–guest systems featuring **1** as an element block is also now under active investigations.

This work was partly supported by a Grant-in-Aid for Scientific Research (M.M., No. 15H00741) on the Innovative Area “Element-Block Polymers (No. 2401)” and (T.Y., No. 15H00941) on the Innovative Area “Stimuli-responsive Chemical Species for the

Creation of Fundamental Molecules (No. 2408)" from MEXT, Japan, and a Grant-in-Aid for Young Scientists (B) from the Japan Society for the Promotion of Science (JSPS) (T.Y., no. 26790001). We would like to thank Prof. Shinjiro Machida and Prof. Takashi Aoki (Kyoto Institute of Technology) for time-resolved fluorescence and optical rotation measurements, respectively.

## Notes and references

<sup>a</sup> Faculty of Molecular Chemistry and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

<sup>b</sup> Faculty of Material Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

<sup>c</sup> Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

<sup>d</sup> National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan.

† Electronic Supplementary Information (ESI) available: Synthetic procedures, NMR spectra, time-resolved fluorescence spectra, and computational studies. See DOI: 10.1039/c000000x/

- (a) H. Maeda, Y. Bando, Y. *Pure Appl. Chem.* 2013, **85**, 1967–1978; (b) K. Watanabe, K. Akagi, *Sci. Technol. Adv. Mater.* 2014, **15**, 044203; (c) J. Kumar, T. Nakashima, T. Kawai, *J. Phys. Chem. Lett.* 2015, **6**, 3445–3452; (d) E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz, S. de la Moya, *Chem.–Eur. J.* 2015, **21**, 13488–13500.
- (a) H. P. J. M. Dekkers, in *Circular Dichroism Principles and Applications*, ed. N. Berova, K. Nakanishi, R. W. Woody, Wiley-VCH, 2000, ch. 7; (b) F. Zinna, L. Di Bari, *Chirality* 2014, **27**, 1–13.
- H. G. Brittain, F. S. Richardson, *J. Phys. Chem.* 1976, **80**, 2590–2592.
- (a) J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, *J. Am. Chem. Soc.* 2003, **125**, 11808–11809; (b) R. Hassey, E. J. Swain, N. I. Hammer, D. Venkataraman, M. D. Barnes, *Science* 2006, **314**, 1437–1439; (c) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa, K. Nozaki, *Org. Lett.* 2013, **15**, 2104–2107; (d) Sawada, Y.; Furumi, S.; Takai, A.; Takeuchi, M.; Noguchi, K.; Tanaka, K. *J. Am. Chem. Soc.* 2012, **134**, 4080–4083.
- (a) T. Kawai, K. Kawamura, H. Tsumatori, M. Ishikawa, M. Naito, M. Fujiki, T. Nakashima, *ChemPhysChem* 2007, **8**, 1465–1468; (b) Y. Tang, A. E. Cohen, *Science* 2011, **332**, 333–336.
- (a) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh, Y. Chujo, *J. Am. Chem. Soc.* 2014, **136**, 3350–3353; (b) M. Gon, Y. Morisaki, Y. Chujo, *J. Mater. Chem. C*, 2015, **3**, 521–529.
- E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, B. G. Vo, G. Muller, S. de la Moya, *J. Am. Chem. Soc.* 2014, **136**, 3346–3349.
- (a) D. E. Koshland, Jr. *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 2375–2378; (b) C. Kremer, A. Lützen, *Chem.–Eur. J.* 2013, **19**, 6162–6196.
- (a) B. Kiupel, C. Niederal, M. Nieger, S. Grimme, F. Vögtle, *Angew. Chem. Int. Ed.* 1998, **37**, 3031–3034; (b) M. Modjewski, S. V. Lindeman, R. Rathore, *Org. Lett.* 2009, **11**, 4656–4659; (c) M. Rickhaus, L. M. Banwart, M. Nuuburger, H. Gsellinger, K. Zimmermann, D. Häussinger, M. Mayor, *Angew. Chem. Int. Ed.* 2014, **53**, 14587–14591; (d) A. Bihlmeier, J. Rotzler, M. Rickhaus, M. Mayor, W. Klopper, *Phys. Chem. Chem. Phys.* 2015, **17**, 11165–11173.
- (a) J. Stahl, J. C. Böhring, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel, F. A. Gladysz, *Angew. Chem. Int. Ed.* 2002, **41**, 1872–1876; (b) L. de Quadras, E. B. Bauer, W. Mohr, J. C. Böhring, T. B. Peters, J. M. Martín-Alvarez, F. Hampel, F. A. Gladysz, *J. Am. Chem. Soc.* 2007, **129**, 8296–8309.
- S. Menning, M. Krämer, B. A. Coombs, F. Rominger, A. Beeby, A. Drew, U. H. F. Bunz, *J. Am. Chem. Soc.* 2013, **135**, 2160–2163.
- (a) H. F. Zobel, *Starch/Stärke*, 1988, **40**, 1–7; (b) W. Hinrichs, G. Büttner, M. Steifa, C. H. Betzel, V. Zabel, B. Pfannemüller, W. Saenger, *Science*, 1987, **238**, 205–208; (c) K. Gessler, I. Usón, T. Takaha, N. Krauss, S. M. Smith, S. Okada, G. M. Sheldrick, W. Saenger, *Proc. Natl. Acad. Sci. USA* 1999, **96**, 4246–4251.
- (a) T. Handa, H. Yajima, *Biopolymers* 1979, **18**, 873–886; (b) T. Handa, H. Yajima, *Biopolymers* 1980, **19**, 723–740.
- (a) Y. Hui, J. C. Russell, D. G. Whitten, *J. Am. Chem. Soc.* 1983, **105**, 1374–1376; (b) O.-K. Kim, J. Je, J. S. Melinger, *J. Am. Chem. Soc.* 2006, **128**, 4532–4533.
- (a) Y. Kaneko, J.-i. Kadokawa, *Chem. Rec.* 2005, **5**, 36–46; (b) M. Ikeda, Y. Furusho, K. Okoshi, S. Tanahara, K. Maeda, M. Nishino, T. Mori, E. Yashima, *Angew. Chem. Int. Ed.* 2006, **45**, 6491–6499; (c) T. Sanji, N. Kato, M. Tanaka, *Org. Lett.* 2006, **8**, 235–238; (d) T. Sanji, N. Kato, M. Tanaka, *Chem.–Asian J.* 2008, **3**, 46–50; (e) M. J. Frampton, T. D. W. Claridge, G. Latini, S. Brovelli, L. Cacialli, H. L. Anderson, *Chem. Commun.* 2008, 2797–2799; (f) T. Kumar, A. J. J. Woortman, K. Loos, *Biomacromolecules* 2013, **14**, 1955–1960.
- (a) G. Wenz, *Angew. Int. Ed. Engl.* 1994, **33**, 803–822; (b) K. Connors, *Chem. Rev.* 1997, **97**, 1325–1358; (c) J. Szejtli, *Chem. Rev.* 1998, **98**, 1743–1753.
- (a) K. Kano, H. Matsumoto, S. Hashimoto, M. Sisido, Y. Imanishi, *J. Am. Chem. Soc.* 1985, **107**, 6117–6118; (b) K. Kano, H. Matsumoto, Y. Yoshimura, S. Hashimoto, *J. Am. Chem. Soc.* 1988, **110**, 2042–2049; (c) M. Inouye, K. Hayashi, Y. Yonenaga, T. Itou, K. Fijimori, T. Uchida, M. Iwamura, K. Nozaki, *Angew. Chem. Int. Ed.* 2014, **53**, 14392–14396.
- (a) K. Kano, N. Tanaka, H. Minamizono, Y. Kawakita, *Chem. Lett.* 1996, 925–926; (b) K. Kano, R. Nishiyabu, T. Asada, Y. Kuroda, *J. Am. Chem. Soc.* 2002, **124**, 9937–9944.
- M. Morisue, S. Ueda, M. Kurasawa, M. Naito, Y. Kuroda, *J. Phys. Chem. A* 2012, **116**, 5139–5144.
- J. Labuta, J. P. Hill, S. Ishihara, L. Hanyková, K. Ariga, *Acc. Chem. Res.* 2015, **48**, 521–529.
- Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jpn.* 2015, **88**, 633–643.
- (a) Y. Kuroda, T. Hiroshige, T. Sera, Y. Shiroiwa, H. Tanaka, H. Ogoshi, *J. Am. Chem. Soc.* 1989, **111**, 1912–1913; (b) Y. Kuroda, M. Ito, T. Sera, H. Ogoshi, *J. Am. Chem. Soc.* 1993, **115**, 7002–7004; (c) K. Kano, R. Nishiyabu, T. Yamazaki, I. Yamazaki, *J. Am. Chem. Soc.* 2003, **125**, 10625–10634; (d) Y. Liu, C.-F. Ke, H.-L. Zhang, J. Cui, F. Ding, *J. Am. Chem. Soc.* 2008, **130**, 600–605; (e) M. Fathalla, A. Neuberger, S.-C. Li, R. Schmehl, U. Diebold, Jayawickramarajah, *J. Am. Chem. Soc.* 2010, **132**, 9966–9967.
- (a) T. Kida, A. Kikuzawa, H. Higashimoto, Y. Nakatsuji, M. Akashi, *Tetrahedron* 2005, **61**, 5763–5768; (b) A. Kikuzawa, T. Kida, Nakatsuji, M. Akashi, *J. Org. Chem.* 2005, **70**, 1253–1261.
- K. W. C. Poon, G. B. Dudley, *J. Org. Chem.* 2006, **71**, 3923–3927.
- See the Supporting Information.
- G. S. Cox, N. J. Turro, N.-c. C. Yang, M.-J. Chen, *J. Am. Chem. Soc.* 1984, **106**, 424–425.
- R. J. Bergeron, M. A. Channing, K. A. McGovern, *J. Am. Chem. Soc.* 1978, **100**, 2878–2883.
- (a) T. Kida, Y. Fujino, K. Miyawaki, E. Kato, M. Akashi, *Org. Lett.* 2009, **11**, 5282–5285; (b) T. Kida, T. Iwamoto, Y. Fujino, T. Tohna, M. Miyata, *Org. Lett.* 2011, **13**, 4570–4573.
- (a) T. Mizutani, T. Kurahashi, T. Murakami, N. Matsumi, H. Ogoshi, *J. Am. Chem. Soc.* 1997, **119**, 8991–9001; (b) X. Hang, Y. Nakanishi, N. Berova, *Chirality* 2000, **12**, 237–255.
- (a) K. Harata, H. Uedaira, H. *Bull. Chem. Soc. Jpn.* 1975, **48**, 375–378; (b) K. Harata, *Bull. Chem. Soc. Jpn.* 1979, **52**, 1807–1812; (c) M. Kodaka, *J. Am. Chem. Soc.* 1993, **115**, 3702–3705.
- A. Ceulemans, W. Oldenhof, C. Görrler-Walrand, L. G. Vanquickenborne, *J. Am. Chem. Soc.* 1986, **108**, 1155–1163.
- F. V. A. Camargo, H. L. Anderson, S. R. Meech, I. A. Heisler, *J. Phys. Chem. A* 2015, **119**, 95–101.
- (a) R. A. Freitag, J. A. Mercer-Smith, D. G. Whitten, *J. Am. Chem. Soc.* 1981, **103**, 1226–1228; (b) R. A. Freitag, D. G. Whitten, *J. Phys. Chem.* 1983, **87**, 3918–3925; (c) K. Konishi, K. Miyazaki, T. Aida, S. Inoue, *J. Am. Chem. Soc.* 1990, **112**, 5639–5640.

A table of contents entry

