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FOCUS REVIEW

The dawn of chiral material development using saccharide-based helical polymers

Tomoyuki Ikai

Polysaccharides, such as cellulose and amylose, are abundant and optically active carbohydrate-based resources. Their suitably modified derivatives (for example, benzoate and phenylcarbamate derivatives) exhibit excellent resolution abilities for a wide variety of chiral compounds when applied to chiral stationary phases (CSPs) for high-performance liquid chromatography. Despite the established application of polysaccharides in CSP materials, their use in other chiral functional materials has been limited. In this review, the author describes the functionalization of cellulose and amylose to yield novel chiral functions other than those in CSPs, as well as the use of these materials for various applications, such as asymmetric organocatalysts, chiral auxiliaries and chiral fluorescent sensors. The synthesis of a saccharide-containing polymer via the polymerization of a glucose-based monomer and its application as a circularly polarized luminescence material are also described.
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INTRODUCTION

To reduce our over dependence on exhaustible fossil resources, the development of new materials from naturally occurring compounds has attracted much interest. Polysaccharides are a series of natural polymers that consist of monosaccharide-based repeating units linked by glycoside bonds. β-1,4- and α-1,4-Glucan polysaccharides, which are known as cellulose and amylose, respectively, are representative examples of these polymers. Cellulose and amylose contain three hydroxyl groups in their glucose repeating units, which are easily derivatized to afford desired functional pendants through polymer reactions with suitable reagents.[1–4] Taking advantage of this important feature, various functions have been appended to cellulose and amylose.[5–12] In fact, many examples of cellulose- and amylose-derived materials are in daily use, including papers, fibers, films, separation filters, superabsorbent resins, cosmetics and food additives.

These polysaccharides, which are inherently optically active, have also been applied to chiral functional materials. Native cellulose and amylose have been used as chiral adsorbents in early studies of chromatographic resolution. However, these materials did not possess sufficient chiral discrimination abilities. In 1951, Kotake *et al.*[13] demonstrated that the resolution of amino-acid derivatives could be achieved using paper chromatography. The groups of Musso[14] and Wulff[15] reported the effectiveness of amylose in the resolution of biphenyl derivatives and menthol, respectively. More useful chiral recognition materials have been obtained through the appropriate modification of cellulose and amylose. Among the large number of derivatives that have been reported, ester and carbamate derivatives (that is, benzoate and phenylcarbamate derivatives) of cellulose and amylose, which have been used as chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC), exhibit excellent resolution abilities for a vast range of chiral compounds.[16–20] The performance of these polysaccharide derivatives in resolution is often better than that of the corresponding oligosaccharide-based materials.[21] This result suggests that the helical chirality derived from the polysaccharide backbone, rather than the central chirality of the repeating glucose units, has a key role in the chiral recognitions. Currently, the resolution using these polysaccharide-based CSPs is indispensable for the analysis of enantiomer compositions as well as the preparation of pure enantiomers, particularly in the pharmaceutical industry.[22,23] However, despite the successful application of cellulose and amylose in CSP materials, their application as other chiral functional materials has been limited.

Therefore, the author has recently focused on exploring novel applications of cellulose and amylose, which exist in great abundance on Earth. In this review, the author primarily presents his studies of the functionalization of cellulose and amylose to impart novel chiral functions as asymmetric organocatalysts,[24] chiral auxiliaries[25] and chiral fluorescence sensors.[26,27] Furthermore, the application of a saccharide-containing polymer, which was prepared by the polymerization of a glucose-based monomer, to a circularly polarized luminescence (CPL) material will also be described.[28] From the perspective of material development, this polymerization approach is very attractive because it allows for unlimited freedom in molecular design and the possibility of creating innovative functional materials.

ASYMMETRIC ORGANOCATALYSTS

Asymmetric organocatalysts have attracted much interest owing to their practical advantages, such as their low environmental burden, low cost and air stability, over common metallic catalysts.[29–33] Amine *N*-oxides are one of the most promising types of organocatalysts

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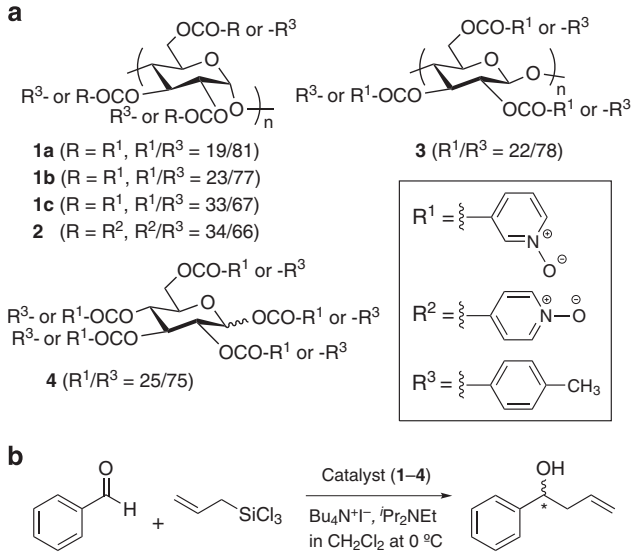

Figure 1 (**a**) Structures of amylose (**1** and **2**), cellulose (**3**) and glucose (**4**) derivatives bearing pyridine *N*-oxide groups. (**b**) Enantioselective allylation of benzaldehyde using allyltrichlorosilane catalyzed by **1**–**4**.

because of their Lewis basicity.[34,35] Various chiral amine *N*-oxides have been developed and applied as chiral organocatalysts in asymmetric reactions (for example, aldol-type reactions, desymmetrization of *meso*-epoxides, cyanosilylation of carbonyl and imine compounds and allylation of aldehydes).[36–40] In 2011, the author reported the first application of cellulose and amylose derivatives as asymmetric organocatalysts.[24] Before that study, the study of polysaccharide-based organocatalysts for asymmetric reactions was limited to chitosan-based materials.[41,42]

The author synthesized amylose (**1** and **2**) and cellulose (**3**) derivatives bearing pyridine *N*-oxide pendants as catalytically active sites and used these compounds as organocatalysts for the asymmetric addition of allyltrichlorosilane to benzaldehyde (Figure 1).[24] The results of the enantioselective allylation reaction using 3-pyridine *N*-oxide-bound amylose derivatives (**1a–c**) with different degrees of substitution are summarized in Table 1 (run 1–3). Increasing the amount of pyridine *N*-oxide in the polymer from 19% (**1a**, run 1) to 23% (**1b**, run 2) resulted in an improvement in the enantioselectivity from 13% enantiomeric excess (ee) to 32% ee. However, a further increase in the number of catalytic sites caused a decrease in the enantioselectivity (24% ee; **1c**, run 3). The corresponding glucose-based catalyst (**4**) exhibited poor and opposite enantioselectivity (8% ee, *S* configuration, run 6) compared with the results obtained using **1**, which indicates the importance of the helical chirality derived from the amylose backbone rather than the central chirality in the repeating glucose units. The influence of the degree of substitution on the enantioselectivity in this allylation is probably due to a slight difference in the higher-order structures of the derivatives. The analogous polymer bearing 4-pyridyl *N*-oxide pendants (**2**) exhibited almost no enantioselectivity (run 4), probably because the catalytically active sites in **2** are located far from the polysaccharide backbone, which indicates that a preferred chiral environment for chiral induction may not be present in **2**. By contrast, the cellulose derivative **3** bearing 3-pyridyl *N*-oxide pendants exhibited catalytic activity in the same allylation reaction (run 5), although their enantioselectivity was lower than that observed for amylose derivative **1b**. Interestingly, the absolute configurations of the predominant enantiomers obtained with **3** were opposite to those obtained using **1b**. This result, combined with the result that **3** exhibited circular dichroism (CD) signals that were opposite to those of **1b** in the absorption region of the aromatic pendants,[24] suggests that the catalytic sites in the amylose and cellulose derivatives are located in mirror image-like environments. This finding reflects the higher-order structures of these polymers and may be the reason for the different enantioselectivities observed in the allylation reactions.

Table 1 Enantioselective allylation catalyzed by polysaccharide (1–3) and glucose (4) derivatives[a]

Run	*Catalyst*	*DS (%)[b]*	*Yield (%)[c]*	*ee (%)[d]*	*Configuration[e]*
1	**1a**	19	47	13	*R*
2	**1b**	23	62	32	*R*
3	**1c**	33	59	24	*R*
4	**2**	34	37	<1	ND
5	**3**	22	70	11	*S*
6	**4**	25	50	8	*S*

Abbreviation: ND, not determined.
[a]Reactions were carried out on a 1 mmol scale in CH_2Cl_2 (2 ml) with allyltrichlorosilane (1.2 equiv.), *N*-oxide (10 mol%), $Bu_4N^+I^-$ (1.2 equiv.) and $^iPr_2NEt$ (5.0 equiv.) for 48 h at 0 °C.
[b]Degree of substitution of pyridine *N*-oxide determined by elemental analysis.
[c]Yield of isolated product.
[d]Determined by chiral HPLC on Chiralcel OD-H.
[e]Absolute configuration of the predominant isomer assigned based on comparison of the optical rotation sign.

CHIRAL AUXILIARIES FOR ASYMMETRIC SYNTHESIS

Asymmetric synthesis using chiral auxiliaries is a powerful technique for preparing optically active compounds in bulk. In contrast to the catalytic approach, a stoichiometric amount of a chiral template is required when chiral auxiliaries are used. Therefore, the chiral auxiliaries must be prepared from inexpensive and abundant chiral natural products. In 1977, Vasella[43] reported a practical chiral auxiliary containing a D-ribose unit. Since that report, various monosaccharide-based chiral auxiliaries have been developed for use in asymmetric reactions, including 1,3-dipolar cycloadditions, 1,4-conjugate additions, Diels–Alder cycloadditions, aza-Friedel–Crafts reactions, alkylations, cyclopropanations and Strecker- and Mannich-type reactions.[44–51] The ready availability of polysaccharides and their potential for use as chiral functional materials make them intriguing scaffolds for chiral auxiliaries. Taking advantage of these factors, the author reported the first example of a polysaccharide-based chiral auxiliary in 2014.[25]

Regioselectively substituted cellulose derivatives bearing 3,5-dimethylphenylcarbamates at the 2- and 3-positions of the glucose unit and a certain bromobenzoate at the 6-position (**5–7**) were synthesized to develop chiral auxiliaries (Figure 2a).[25] In addition, the corresponding randomly substituted cellulose derivative (**9**) bearing 2-bromobenzoate at some of the 2-, 3- and 6-positions was also prepared. These derivatives were used as chiral auxiliaries for the asymmetric synthesis of biaryl compounds **12–14** using a Suzuki–Miyaura cross-coupling with naphthalen-1-ylboronic acid **11**, followed by quantitative hydrolysis and methyl esterification (Figure 2b and Table 2). Consistent with the previously mentioned study of polysaccharide-based asymmetric organocatalysts, polysaccharide-based **5** exhibited better performance (17% ee, run 1) than the corresponding glucose-based material (**10**) (3% ee, run 6). When non-regioselectively substituted **9** (run 5) was used as the chiral auxiliary, the ee of the product decreased to 5%. Because **9** has the same pendant units (R^1 and R^4) as **5** and the compositions of the two auxiliaries were nearly the same, the chiral environment around the 6-position in the helical structure may be more suitable for

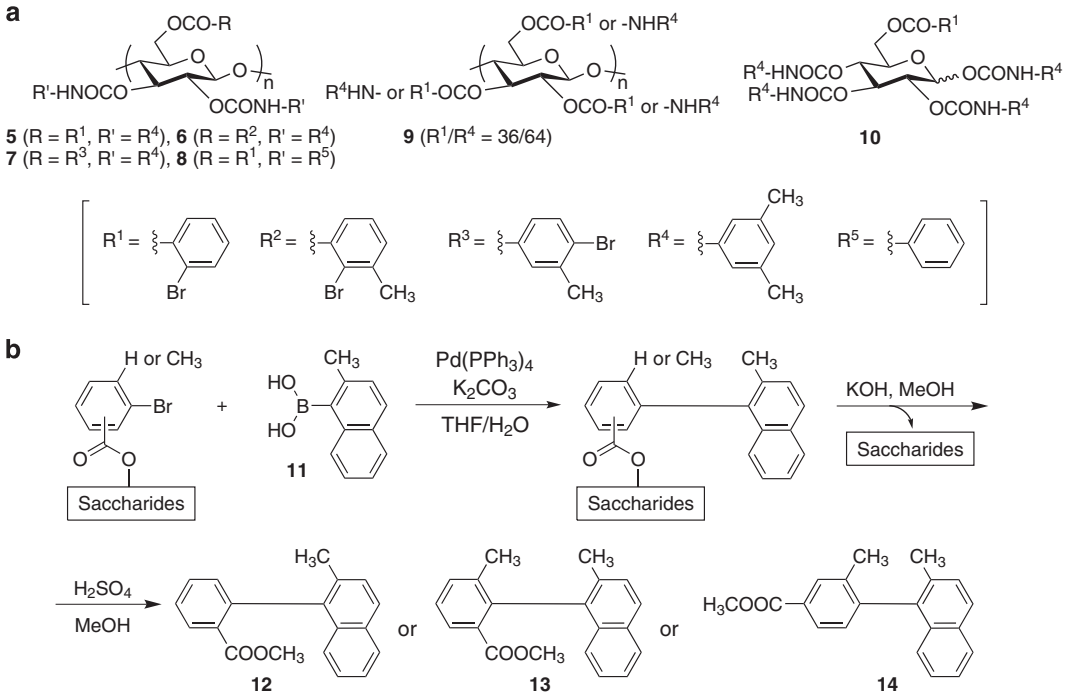

Figure 2 (**a**) Structures of cellulose (**5**–**9**) and glucose (**10**) derivatives bearing bromobenzoate pendants. (**b**) Synthesis of optically active biaryl compounds (**12**–**14**) using saccharide-based chiral auxiliaries and naphthalen-1-ylboronic acid (**11**).

diastereoselective Suzuki–Miyaura cross-coupling than the environments around the 2- and 3-positions. The polymer with non-substituted phenylcarbamate pendants at the 2- and 3-positions of the glucose unit (**8**) afforded **12** with the highest ee value (24% ee, run 4) among the studied polysaccharide-based auxiliaries.

CHIRAL FLUORESCENT SENSORS

Chiral discrimination using fluorescence responses as output signals is considered to be one of the most practical techniques for discriminating molecular chirality because of its simplicity, rapidity, high sensitivity and high-throughput ability.[52] To date, various chiral fluorescent sensors have been developed based on small molecules, such as bis(oxazolinyl)phenol-, helicene-, 1,8-diheteroarylnaphthalene- and binaphthyl-based compounds, and synthetic polymers.[52–55] These reported sensors can only be applied to chiral compounds with either central or axial chirality except for a few examples.[56–58] Because the number of chiral molecules is increasing each day, the development of powerful chiral fluorescent sensors that exhibit good enantioselectivity toward various types of chirality is highly desired. Because polysaccharide derivatives that are used as CSPs for HPLC exhibit excellent enantioselectivity toward a wide variety of chiral compounds, the author recently developed novel polysaccharide-based chiral fluorescence sensors, which successfully recognized different types of chirality (for example, central and axial chirality).[26,27]

Phenylcarbamate derivatives of cellulose (**15**) and amylose (**16**) bearing terthienyl-based π-conjugated pendants as fluorescent signaling units at the 2-, 3- and 6-positions of the glucose unit were synthesized for use as chiral fluorescent sensors (Figure 3).[26,27] Bulky branched alkyl chains were introduced at the terminal thiophene ring of the π-conjugated pendants to increase their affinity for nonpolar solvents, such as hexane. **15** and **16** are soluble in common organic solvents, such as chloroform and tetrahydrofuran (THF), as well as mixtures of these solvents with 90 vol% hexane. Based on dynamic light scattering analysis, aggregate formation did not occur in a hexane/THF (90/10, v/v) mixed solvent. The solubility in less polar solvents has important implications for sensing applications, as described below.

Table 2 Enantioselective synthesis of biaryl compounds using saccharide-based chiral auxiliaries (5–10)[a]

Run	*Chiral auxiliary*	*Conv. (%)[b]*	*Predominant product*	*ee (%)[c]*
1	**5**	72	(*R*)-**12**	17
2	**6**	<5	ND[d]	ND[d]
3	**7**	83	(*R*)-**14**	4
4	**8**	75	(*R*)-**12**	24
5	**9**	70	(*R*)-**12**	5
6	**10**	>99[e]	(*R*)-**12**	3

Abbreviation: ND, not determined.
[a]Suzuki–Miyaura cross-coupling reactions were carried out with chiral auxiliary (1.0 equiv.), boronic acid (2.5 equiv.), $Pd(PPh_3)_4$ (0.2 equiv.) and K_2CO_3 (10 equiv.) in THF/water (2/1, v/v) for 48 h at 75 °C.
[b]Conversion ratios from bromobenzoates to biaryl pendants.
[c]Enantiomeric excess of the product determined by chiral HPLC on Chiralcel OD-H.
[d]Could not be determined because of very low conversion.
[e]Determined from the ^{1}H NMR spectrum of the reaction system after cross-coupling.

Figure 4a shows the CD and absorption spectra of **15** and **16** in a hexane/THF (90/10, v/v) mixed solvent. Notably, the CD spectral patterns of **15** and **16** are nearly mirror images of each other, which indicates that the terthienyl-based pendants in the polymers are arranged in opposite chiral environments. The characteristic split-type CD patterns indicate that the π-conjugated pendants of **15** and **16** are arranged in a clockwise and counterclockwise twisting manner, respectively, along the main chains, which possess left-handed 3/2 and 4/3 helical conformations, respectively.[18,20] The fluorescence spectra of **15** and **16** in hexane/THF (90/10, v/v) are shown in Figure 4b. Photographs of the solutions under irradiation at 365 nm are also shown, and apparent greenish emissions that are derived from the

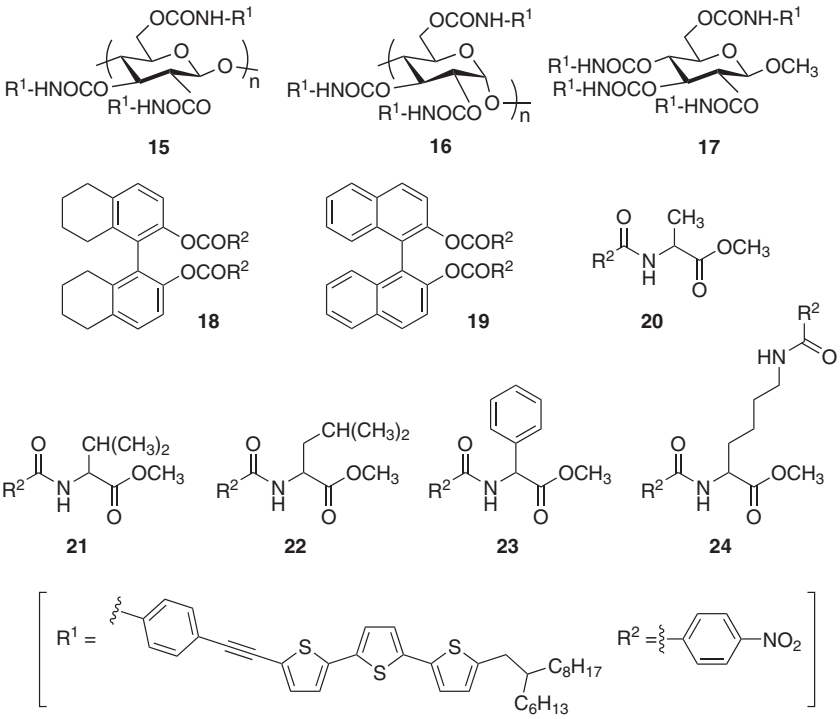

Figure 3 Structures of cellulose (**15**), amylose (**16**) and glucose (**17**) derivatives bearing terthienyl-based pendants and aromatic nitro compounds (**18**–**24**).

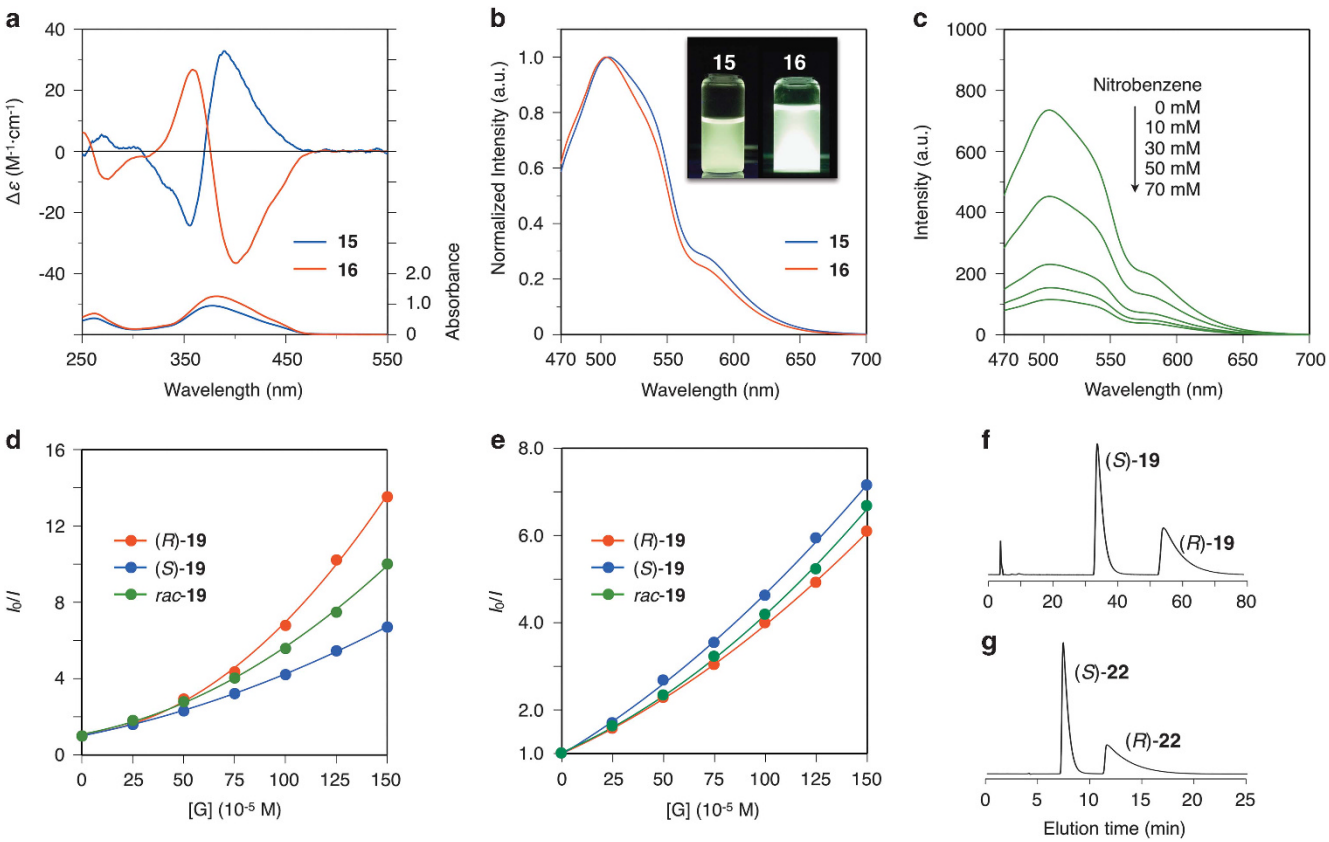

Figure 4 (**a**) CD and absorption spectra of **15** and **16** in hexane/THF (90/10, v/v) at 25 °C. (**b**) Fluorescence spectra of **15** and **16** in hexane/THF (90/10, v/v) at room temperature (λ_{ex} = 450 nm). The inset shows photographs of the solutions under irradiation at 365 nm. (**c**) Fluorescence spectra of **15** upon addition of various amounts of nitrobenzene (0–70 mM) in hexane/THF (90/10, v/v) at room temperature (λ_{ex} = 450 nm). (**d**, **e**) Stern–Volmer plots for fluorescence quenching of **15** (**d**) and **16** (**e**) by (*R*)-**19** (red) and (*S*)-**19** (blue) in hexane/THF (90/10, v/v) at room temperature. The results using *rac*-**19** as a quencher are also shown (λ_{ex} = 450 nm). (**f**, **g**) Chromatograms for resolutions of **19** (**f**) and **22** (**g**) on a **15**-based CSP (column, 25 cm × 0.20 cm (i.d.); eluent, hexane/2-propanol (90/10, v/v); flow rate, 0.2 ml min^{-1}). Reproduced from the study by Ikai *et al.*[26,27] with permission.

terthienyl-based pendants were observed in both cases. When nitrobenzene was added to solutions of **15**, the greenish emission was quenched, which was probably due to photoinduced electron transfer from the π-conjugated pendants to nitrobenzene (Figure 4c).

A decrease in the fluorescence intensity of **15** was also observed when chiral aromatic nitro compounds (**18–24** in Figure 3) were used as fluorescence quenchers. The Stern–Volmer plots for fluorescence quenching of **15** by the (*R*)- and (*S*)-isomers of **19** are shown in Figure 4d, and the results indicate that (*R*)-**19** quenched the emission of **15** more efficiently than (*S*)-**19**. An intermediate quenching between those obtained with (*R*)-**19** and (*S*)-**19** was observed when *rac*-**19** was used as a quencher. In addition, **15** exhibited apparent enantioselective fluorescence responses toward various types of aromatic nitro compounds (**19–24**) with either central or axial chirality in hexane/THF (90/10, v/v). In all cases, the fluorescence emission from **15** was more strongly quenched by the (*R*)-isomer, which indicates that the intermolecular interactions between **15** and the (*R*)-isomers are more effective than those with the corresponding (*S*)-isomers. By contrast, the corresponding glucose derivative (**17**) exhibited almost no chiral fluorescence sensing ability. These results indicate that the one-handed helical structure of **15** has an indispensable role in its chiral fluorescence-sensing ability. Increasing the proportion of THF in the solution of **15** led to a decrease in the ability of aromatic nitro compounds to quench the fluorescence, and the difference in the degree of quenching between enantiomers became small. Therefore, hydrogen bonding and/or dipole–dipole interactions between the carbamate groups of the fluorophores and the nitro group of quenchers appear to be important for efficient fluorescence quenching.

The chiral recognition ability of **15** toward **18–22** was also evaluated using **15** as a CSP for HPLC. Baseline resolutions of *rac*-**18–22** were achieved using the **15**-based CSP, and in all cases, the (*S*)-isomers eluted first followed by the (*R*)-isomers. Two examples are shown in Figures 4f and g. This result suggests that **15** interacts more strongly with the (*R*)-isomers than with the corresponding (*S*)-isomers during the resolution, and this enantioselectivity is in agreement with the fluorescence-sensing results. Comparison with the resolution ability of the cellulose tris(phenylcarbamate) (CTPC)-based CSP indicates that the terthienyl-based pendant in **15** provides fluorescent functionality as well as an attractive chiral recognition site, which occasionally affords more efficient chiral discrimination than that achieved with CTPC.[59]

16 also exhibited enantioselective fluorescence quenching toward aromatic nitro compounds (**19–24**), but the observed enantioselectivity was opposite to that obtained with cellulose-based **15**.[27] For example, the Stern–Volmer plot for chiral fluorescence sensing of **19** using **16** is shown in Figure 4e. This opposite enantioselectivity in the fluorescent sensing may result from the π-conjugated pendants in **16** being arranged in chiral environments opposite to those of **15**, as discussed above.

CIRCULARLY POLARIZED LUMINESCENCE MATERIALS

Various organic compounds with interesting molecular structures exist in nature, and some of these structures cannot yet be synthesized in the laboratory. The incorporation of unique structural features of naturally occurring products into molecular designs is intriguing because it enables the creation of otherwise unimaginable materials. Ellagitannin is a series of natural compounds bearing one or more biphenyl units linked to a sugar unit.[60,61] These molecules are optically active owing to the chiral centers in the sugar moiety and the chiral axis in the biphenyl unit. Despite this interesting structural feature,

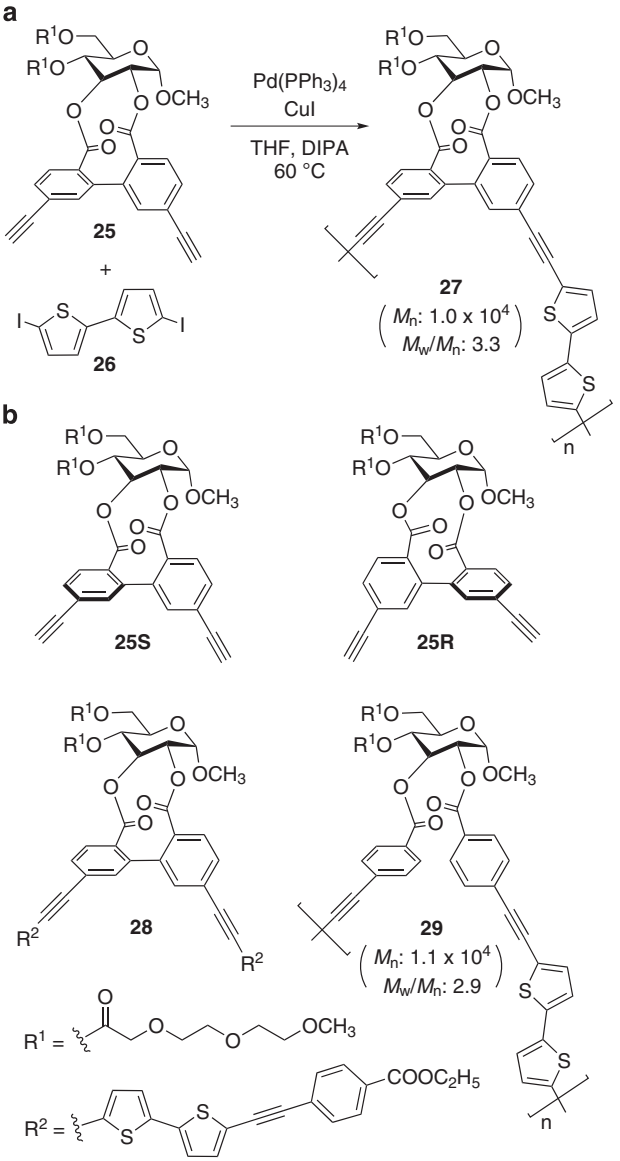

Figure 5 (**a**) Synthesis of **27** using a Sonogashira–Hagihara coupling reaction between **25** and **26**. (**b**) Structures of **25S**, **25R**, **28** and **29**.

ellagitannin has not yet been used as a building block for chiral functional materials. Inspired by naturally occurring ellagitannins with chirally twisted biphenyl units, the author designed and synthesized an original diethynyl monomer (**25**) bearing a glucose-linked biphenyl unit to prepare a helical saccharide-containing polymer (Figure 5).[28] ^{1}H nuclear magnetic resonance and chiral HPLC analyses of **25** revealed that the axial chirality of the biphenyl unit was dynamic. In addition, **25** was in equilibrium between **25S** and **25R**, which have opposite twist handedness. The diastereomeric ratio was estimated to be 94:6 in favor of **25S** in chloroform. A Sonogashira–Hagihara coupling reaction between **25** and **26** provided optically active **27**, which contains a glucose-based repeating unit in the main chain. The axial chirality of the biphenyl units of **27** was biased in favor of the (*S*)-configuration at the same ratio as the equilibrium mixture of **25** in chloroform. The CD intensity of **27** in chloroform/acetonitrile increased as the acetonitrile content of the solution increased, which was accompanied by a clear hypochromic effect in the absorption spectrum (Figure 6a). In marked contrast, the CD and absorption

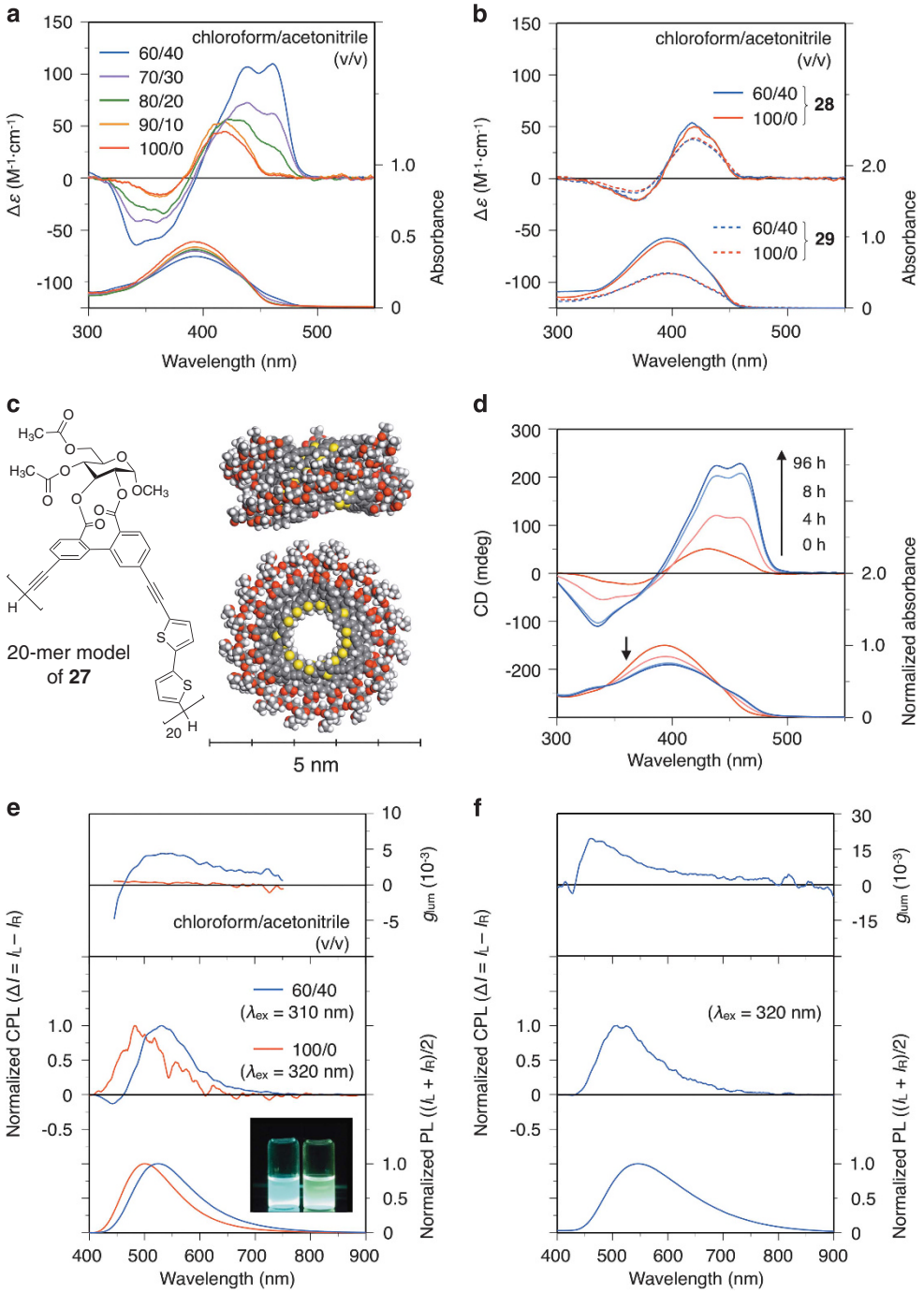

Figure 6 (**a**, **b**) CD and absorption spectra of **27** (**a**) and **28** and **29** (**b**) in chloroform/acetonitrile (100/0–60/40, v/v) at 25 °C. [glucose unit] = 1.0×10^{-4} M. (**c**) Side view (top) and top view (bottom) of a model of a possible left-handed helical structure of **27** (20 mer). (**d**) Time-dependent CD spectral changes of a chloroform-cast film of **27** upon exposure to acetonitrile vapor. (**e**, **f**) photoluminescence (bottom), CPL (middle) and g_{lum} (top) spectra of **27** in chloroform/acetonitrile (100/0 or 60/40, v/v) (**e**) and a chloroform-cast film of **27** after exposure to acetonitrile vapor for 96 h (**f**) at room temperature. Reproduced from the study by Ikai *et al.*[28] with permission.

spectra of **28** and **29**, which are monomeric and polymeric model compounds of **27**, respectively, did not exhibit an apparent solvent dependency (Figure 6b). These findings indicate that **27** can alter its backbone conformation in response to the solvent environment and behave as a foldamer,[62–69] which is defined as a synthetic oligomer or polymer that can only fold into a well-defined compact conformation in a specific environment. **27** is expected to fold into a preferred-handed helical conformation in solutions that contain large amounts of a poor solvent (for example, acetonitrile). A solvophobic interaction between aromatic units seems to be essential for the promotion of helical folding and the stabilization of the helical conformation. Based on the molecular weight dependence of the chiroptical properties and the plausible helical structure estimated in a computational study (Figure 6c), cooperative intramolecular

interactions along eight turns of the helix are required for sufficient stabilization of the helically folded state of **27** in a chloroform/acetonitrile mixture (60/40, v/v). The biphenyl framework linked to the glucose units most likely affords moderate rigidity to the polymer backbone and has an important role in the construction of a specific helical conformation.

The film-state chiroptical properties of **27** were also investigated. As expected, the film of **27** prepared from a chloroform/acetonitrile mixture (60/40, v/v) exhibited a more intense CD signal than that from the chloroform-cast film. Interestingly, when the chloroform-cast film of **27** was maintained under saturated acetonitrile vapor at room temperature, its CD and absorption spectra gradually changed with the exposure time, and a substantial increase in the CD intensity and a hypochromic effect in the absorption were observed (Figure 6d). After exposure for 96 h, the CD intensity was comparable to that of the cast film that was prepared directly from the mixed chloroform/acetonitrile system. This result indicates that the structural transition of the backbone of **27** from a random coil to a helical state is possible by solvent vapor annealing even in the film.

To develop a foldamer-based advanced material that is capable of changing its performance through a folding/unfolding transition, the relationship between the CPL properties and the backbone conformations of **27** was investigated. The CPL emission of **27** was greenish in color, and its magnitude varied depending on the solvent used. As expected from the results of the CD analysis, **27** exhibited superior CPL emission in a chloroform/acetonitrile (60/40, v/v) mixture compared with that in chloroform. The CPL dissymmetry factor ($g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the photoluminescence intensities of the left- and right-handed circularly polarized light, respectively) in the mixed solvent system reached 4.5×10^{-3}. This value is 15 times higher than that estimated for the chloroform solution. The CPL emissions of **28** and **29** exhibited almost no solvent dependence, and the g_{lum} values in chloroform/acetonitrile (60/40, v/v) were estimated to be 0.4×10^{-3} and 0.6×10^{-3}, respectively. This result indicates that the helically folded conformation is a necessary prerequisite for efficient CPL emission. Furthermore, a film of **27** exhibited a g_{lum} value of 1.9×10^{-2} after exposure to acetonitrile vapor for 96 h (Figure 6f). This value is sufficiently high compared with those obtained for previously reported preferred-handed helical polymers in non-oriented films and molecularly dispersed solutions.[70–76] The intermolecular couplet of the helically folding **27** may also contribute to the expression of the efficient CPL performance.

CONCLUSIONS

In this review, the author has outlined results from his latest studies on functionalized polysaccharides and saccharide-containing polymer for application in chiral materials other than CSPs. To date, the author and co-workers have succeeded in discovering new potential applications for these polymers in asymmetric organocatalysts, chiral auxiliaries, chiral fluorescence sensors and CPL materials. Although the performance of these materials may not be satisfactory compared with those of previously reported materials that are not derived from polysaccharides, the author believes that this research illustrates the distinct possibility of utilizing the chirality of abundant biomass resources in future functional materials. In addition, the results obtained in these studies reveal the next challenge in this field, which is related to the following simple question: 'Why do certain polysaccharides show better performance than other polysaccharides?' To develop practical polysaccharide-based materials, researchers must seriously address this issue and clarify the correlation between the higher-order structures of polysaccharides and their expression of chiral functionalities.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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