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FOCUS REVIEW

Polymer-based supramolecular sensing and application to chiral photochemistry

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Supramolecular sensing using polymers is of particular significance not only for fundamental science but also for a number of practical diagnostic applications because, upon interaction with target analytes, polymers are capable of amplifying the binding events and thus greatly enhance the signal gain. Hence, we proposed the construction of supramolecular sensors based on chiral functional polymers, such as synthetic conjugated polymers and modified polysaccharides, which are responsive to biologically important chiral materials and saccharides. The present strategy using polymer hosts that behave very differently from those commonly employed in conventional chemosensors is based on the chirality or molecular information propagation and amplification in the polymer chains. By exploiting the knowledge and techniques obtained from the polymer-based supramolecular sensing of bio-related materials, we have expanded the research to photochemical asymmetric synthesis, or 'photochirogenesis,' which provides ecologically benign yet versatile routes to optically active compounds via electronically excited states and is also one of the most attractive and challenging topics in current chemistry. In this review, the author highlights polymer-based supramolecular sensing and application to photochirogenesis with recent examples.
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INTRODUCTION

The construction of supramolecular- (chirality) sensing systems for essential biomolecules, such as amino acids, peptides and saccharides, is one of the most crucial and challenging topics in current chemistry and thus is of particular significance.[1–12] Particularly, polymer-based supramolecular chirality-sensing systems have recently attracted much attention not only in basic science but also in practical applications because of the increasing demand for optically active compounds in the fields of pharmaceutical, medicinal, agricultural and other chemistry-related science and technology.[13–18] This is because conjugated polymers often amplify the signal response, that is, the efficient quenching of the fluorescent polymers, and greatly enhance the signal obtained upon interactions with target guests.[19–22]

By sufficiently utilizing the advantages of polymer hosts, we have developed not only supramolecular chirality sensory systems by using polythiophene (PT) backbones for amino acids and peptides[23–25] but also glucan-based supramolecular oligosaccharide sensors that are operative in aqueous media.[26,27] This strategy is based on the synchronized conformational changes in the polymer backbones induced upon complexation with such bio-related analytes, which is a conceptually different methodology from that of the previously reported sophisticated chiral and saccharide sensors,[1–22] as noted below.

To further progress supramolecular sensing using polymer hosts in the ground state, we have expanded the study to polymer-based chiral photochemistry, or 'photochirogenesis,' in which asymmetric induction occurs in electronically excited states. Photochirogenesis[28–33] enables access to the thermally forbidden routes toward enantiomerically pure compounds and is thus an attractive alternative to the conventional catalytic and enzymatic asymmetric syntheses in the ground state; however, photochirogenesis still remains a challenge in current boundary areas of polymer chemistry and photochemistry. Hence, we opted to expand the conventional molecular and supramolecular photochirogeneses to polymer-based photochirogenesis by using polysaccharides as a chiral scaffold and a molecular host.[34–36]

In this review, the author describes the principles, structure designs and results of PT- and curdlan (Cur) -based supramolecular-sensing hosts in the ground state. Then, chiral photochemistry using polysaccharides in the excited state will be presented. These results will be discussed to elucidate the factors that control supramolecular-sensing and photochirogenic processes with flexible polymer backbones.

POLYTHIOPHENE-BASED SUPRAMOLECULAR CHIRALITY SENSING

In this section, we chose the conjugated polymer PT as a backbone that is conformationally flexible upon structural changes to develop a chirality-sensing supramolecular system because Swager and co-workers demonstrated that a crown ether-PT conjugate showed remarkably high sensitivities and selectivities toward achiral cations.[37,38] The basic principle of the present amplification-sensing strategy is schematically illustrated in Scheme 1. A chirality- or molecular-sensing moiety is attached to the conformationally flexible PT as a signal-amplifying, non-chiroptical reporter, which is originally

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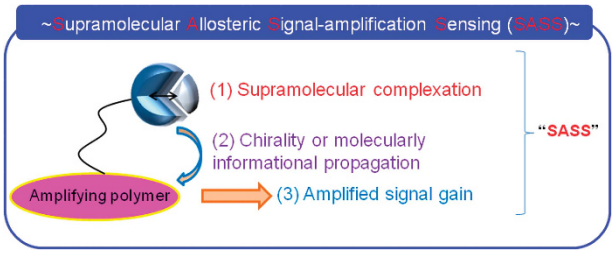
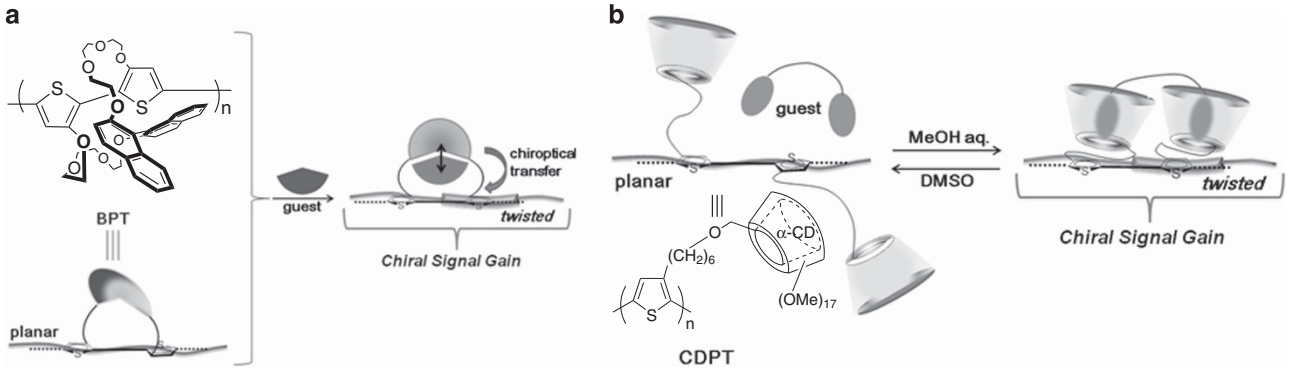
planar. When a (chiral) guest binds to a size-fitted host moiety with supramolecular interactions (1), chirality or molecular information allosterically propagates to the signal-amplifying PT (2), causing synchronized conformational changes of the PT backbone with an accompanying hypsochromic shift, that is, twisting, to afford an amplified signal gain from the amplifying PT reporter (3). The author defines these processes, (1)–(3), as supramolecular allosteric signal-amplification sensing (SASS). The present SASS strategy for sensing the guest chirality or molecular information is different from those commonly used in conventional sensors,[1–22] in which the direct changes in the signal of a chromophore are intended to be read out. Although sophisticated chirality memory systems using chromophoric polyphenylacetylenes (reported by Yashima *et al.*[9,15,18]) and allosteric molecular catalysts[39] and hosts[5,40] are well known, the author wants to emphasize that the present sensing strategy is capable of quantifying an accurate amount of substance from an association constant as well as the enantioselectivity upon complexation by easily and quickly monitoring the UV and/or fluorescence signals, rather than by using a high-cost circular dichroism (CD) instrument.

To experimentally demonstrate the SASS principle, we synthesized binaphthocrown ether-PT (BPT; Scheme 2a) and cyclodextrin-PT (CDPT; Scheme 2b) conjugates. First, the author wishes to introduce chirality sensing by BPT.[23,24] The basic idea for amplifying the chirality-sensing ability of BPT is illustrated in Scheme 2a. Based on the SASS concept, the originally planar PT moiety is twisted upon the inclusion of a chiral guest by the oxyethylene moieties, accompanied by a hypsochromic shift and amplified chiroptical signals. BPT was synthesized in 22% yield (based on the monomer units) by polymerization of the corresponding monomer, which was prepared from 3-bromothiophene in six steps, with $Fe(acac)_3$ as a catalyst. The number average molecular weight (M_n) and the polydispersity index of the BPT thus obtained were 3400 and 1.6, respectively, determined by gel permeation chromatography measurements. However, it is noted that a higher molecular weight segment was detected above the upper limit of the gel permeation chromatography column used, and hence, the real M_n may be higher. The chiroptical properties of BPT were examined in dichloromethane (DCM) by UV/vis and CD spectroscopies. As shown by the red line in Figure 1a, the major ^1B_b band of the attaching binaphthyl chromophore in BPT exhibits an intense negative exciton coupling of the molar CD ($\Delta\varepsilon$) at 240 nm ($-133\ M^{-1}\ cm^{-1}$), while the UV/vis spectrum of BPT exhibits a π–π^* transition of the PT main chain at 400–680 nm, showing an extremely weakly induced positive Cotton effect ($\Delta\varepsilon$ of $<0.06\ M^{-1}\ cm^{-1}$) that is probably due to the flexible oxyethylene linkers connecting the binaphthyl groups in BPT. To obtain the chiral recognition ability, we investigated the binding behavior of BPT with the methyl esters of enantiopure alanine (Ala-OMe•HCl), valine (Val-OMe•HCl), leucine (Leu-OMe•HCl), proline (Pro-OMe•HCl) and phenylalanine (Phe-OMe•HCl) as cationic chiral guests in DCM. In Figure 1a, the gradual addition of each chiral guest to a DCM solution of BPT caused a small but steady hyperchromic effect at shorter wavelengths (350–390 nm) and a hypochromic effect at longer wavelengths (>400 nm), with the accompanying isosbestic point at 395 nm in the UV/vis spectra. These hypsochromic shifts indicate that the PT backbone is twisted upon the inclusion of the chiral guest. Therefore, we can determine the association constants (K_L or K_D) by nonlinear least-squares fitting assuming a 1:1 stoichiometry and the enantioselectivities (K_D/K_L) of all the chiral guests, examined from the UV/vis signal gain only, that is, without using a CD spectrometer. Comparing the enantioselectivities and sensitivities obtained for Ala-OMe•HCl upon complexation with the corresponding monomer and BPT, both hosts showed comparable enantioselectivities of 2.1 and 2.4, respectively, despite employing the same sensing unit. Of particular importance, the actual quantity of analyte required for appreciable detection is two orders of magnitude smaller for BPT than for the monomer, which indicates that BPT has microgram sensitivity. It is noteworthy that BPT acts as a high-sensitivity, chirality-sensing polymer for amino acid derivatives, particularly for Val-OMe•HCl, which exhibits the highest enantioselectivity of 7.3 among the amino acids examined. We have therefore demonstrated that the SASS concept is effective by only reading out the UV/vis absorption changes of the achiral PT backbone through supramolecular chiral interactions rather than the CD spectral changes.[23]

We further expanded the scope of the SASS strategy for chirality sensing to the inherently more sensitive fluorescence spectroscopy by using BPT as a fluorescent chirality-sensing host and (*R*)- and (*S*)-α-methyl-4-nitrobenzylamine hydrochloride (MNBA) as an enantiomeric fluorescence quenching guest pair. The chiral recognition



Scheme 1 SASS: principle and mechanism of signal transfer and propagation to an amplifying polymer.



Scheme 2 SASS-based polythiophenes: schematic drawings of the concept and mechanism of chirality sensing by (**a**) BPT and (**b**) CDPT. A full color version of this scheme is available at *Polymer Journal* online.

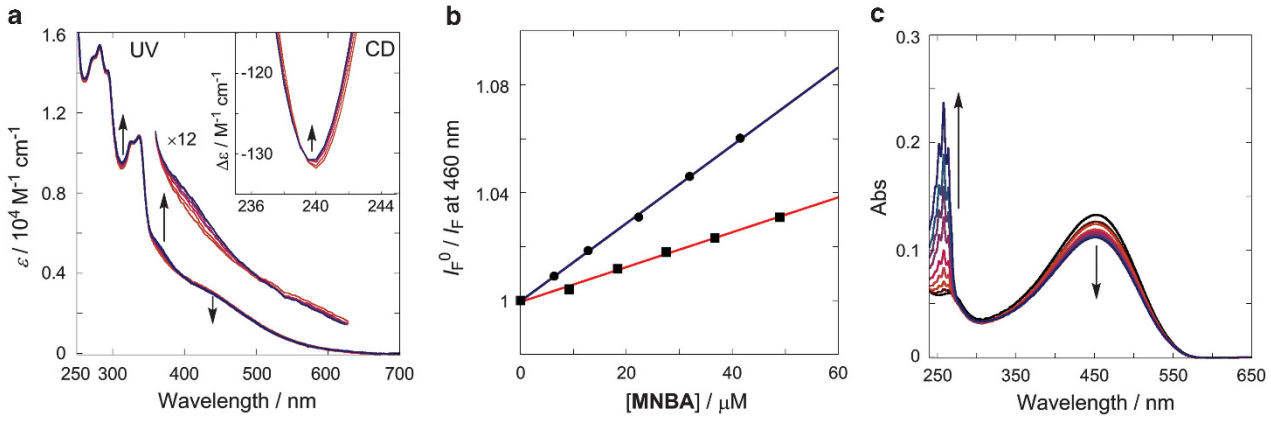


Figure 1 (**a**) UV/vis spectral changes of a DCM solution of BPT (19 μM in a monomer unit) upon gradual addition of D-Ala-OMe•HCl (0–78.7 μM; from red to blue) at 25 °C; the inset shows the CD spectral changes (original data from Fukuhara and Inoue[23]). (**b**) Stern–Volmer plots of the fluorescence quenching of BPT (21 μM in a monomer unit) by (*R*)-MNBA (circle) and (*S*)-MNBA (square) at room temperature (original data from Fukuhara and Inoue[24]). (**c**) UV/vis spectral changes of a 50% aqueous methanol solution of CDPT (24.2 μM in a monomer unit) upon gradual addition of L-Phe-OMe•HCl (0–0.0943 mM; from black to blue) at 25 °C (original data from Fukuhara and Inoue[25]).

behavior of BPT with the enantiomeric MNBA was first investigated by conventional UV/vis spectroscopy as mentioned above. The gradual addition of a DCM solution of BPT caused similar hyperchromic and hypochromic effects, with an isosbestic point at 395 nm, indicating that the PT backbone twists upon complexation with MNBA to give the ground-state association constants of $K_R = 283\,000\ M^{-1}$ and $K_S = 131\,000\ M^{-1}$ for (*R*)- and (*S*)-MNBA, respectively, and an enantioselectivity of $K_R/K_S = 2.16$. To examine the excited-state behavior of the BPT•MNBA complex, we performed steady-state fluorescence spectral titration of the same BPT solution with the enantiomeric MNBA pair, in which BPT was excited at the isosbestic point (that is, at 395 nm), where MNBA has no absorption. The BPT fluorescence was quenched by both enantiomers, but the quenching efficiency was appreciably higher for (*R*)- than for (*S*)-MNBA, in accordance with the UV/vis titration results. As shown in Figure 1b, the fluorescence titration data were subjected to Stern–Volmer analysis and gave excellent straight lines for both enantiomers. From the slope of the straight lines, the Stern–Volmer constants ($k_q\tau^0$) for (*R*)- and (*S*)-MNBA were determined as 1450 and 650 M^{-1}, respectively. From these values, we can calculate the enantioselectivity in the excited-sate k_{qR}/k_{qS} (2.23), which nicely coincides with the ground-state enantioselectivity of K_R/K_S (2.16). This agreement seems reasonable if the fluorescence quenching is static in nature and occurs with exactly the same rate constant in the diastereomeric BPT•MNBA complex pair. To further elucidate the fluorescence quenching kinetics, we determined the fluorescence lifetime of BPT ($\tau^0 = 2.6$ ns) with the time-correlated single-photon-counting method and therefore obtained the fluorescence quenching rate constants for (*R*)- and (*S*)-MNBA ($k_{qR} = 5.6 \times 10^{11}$ and $k_{qS} = 2.5 \times 10^{11}\ M^{-1}\,s^{-1}$). These values are more than one order of magnitude greater than the diffusion-controlled rate constant in DCM ($k_{diff} = 1.5 \times 10^{10}\ M^{-1}\,s^{-1}$), revealing that the quenching process is absolutely static. These results show that the intracomplex fluorescence quenching is extremely fast and nonenantioselective even if the BPT•MNBA complex is a pair of diastereomers, and hence, the nonunity relative quenching constant k_{qR}/k_{qS} (2.23) is ascribed solely to the relative affinity K_R/K_S (2.16). The SASS strategy can be further expanded to chirality sensing of various quenching analytes and can therefore be used to sense other quenching guests that are difficult to detect using the conventional absorption or chiroptical signal gain.[24]

Finally, the author would like to explain the extended scope of the SASS concept in aqueous solution for the sensing of biologically important dipeptides, that is, CDPT, as shown in Scheme 2b.[25] We chose PT as the signal-amplifying reporter and permethyl-α-cyclodextrin, which is known to bind various biological guests such as amino acids and peptides in aqueous solution. The CDPT sensing following the SASS principle is described in Scheme 2b: in aqueous media, the water-soluble cyclodextrin moieties interact weakly with the hydrophobic PT main chain without causing significant conformational changes in the polymer backbone. When the cyclodextrin pendant includes an organic guest, the whole complex becomes bulkier and more hydrophobic and is expected to aggregate with the hydrophobic PT chain, thus causing appreciable conformational changes that can be monitored by UV/vis spectroscopy. CDPT was synthesized in 44% yield by the polymerization of α-cyclodextrin-appended thiophene monomers prepared from 2,5-dibromo-3-(6-bromohexyl)thiophene with a [Ni(dppp)Cl_2] catalyst. The M_n and polydispersity index were determined by gel permeation chromatography analysis to be 34 500 and 1.9, respectively. The chiroptical properties of CDPT were examined in dimethylsulfoxide (DMSO), methanol and 50% aqueous methanol by means of UV/vis and CD spectroscopies. The UV/vis spectra of CDPT in the various solvents used show a π–π* transition of the PT main chain centered at 450 nm, a region in the CD spectra where induced weak Cotton effects generally occur. However, the Cotton effect pattern is appreciably solvent-dependent, showing a broad positive peak ($\Delta\varepsilon = \sim 0.1\ M^{-1}\,cm^{-1}$) in DMSO and apparent positive couplets in pure and aqueous methanol ($\Delta\varepsilon = \sim \pm 0.1\ M^{-1}\,cm^{-1}$), indicating that the remote chiral auxiliary, permethyl-α-cyclodextrin, attached to PT through a flexible hexamethylene tether, can interact with the achiral PT main chain in a right-handed helical conformation in methanolic solvents probably via hydrophobic interactions. To investigate the binding and chiral discrimination behavior of CDPT, we performed titration experiments with enantiomeric Phe-OMe, tryptophan methyl ester (Trp-OMe), histidine (His), tyrosine (Tyr) and 4-nitrophenylalanine (4-NO_2-Phe) as well as with the dipeptides Phe–Phe, Phe–Trp, Gly–Tyr and Tyr–Tyr in 50% aqueous methanol. In Figure 1c, the gradual addition of the amino acid derivatives or dipeptides to a 50% aqueous methanol solution of CDPT caused an apparent hyperchromic effect at shorter wavelengths and a steady hypochromic effect with a slight

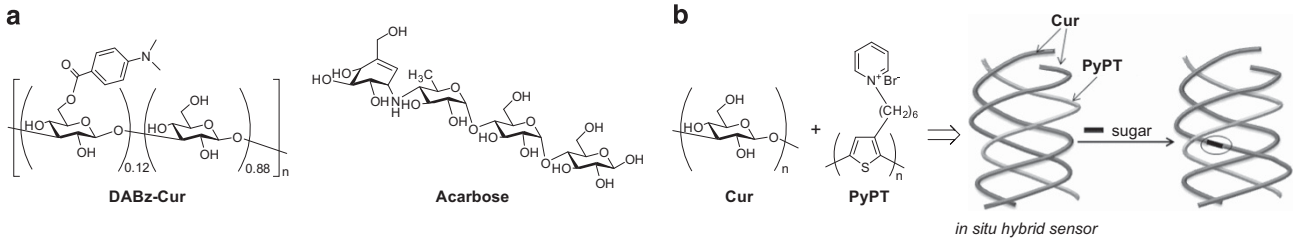


Figure 2 Chemical structures of (**a**) DABz-Cur and acarbose and (**b**) native Cur, PyPT and their hybrid triplex. A full color version of this figure is available at *Polymer Journal* online.

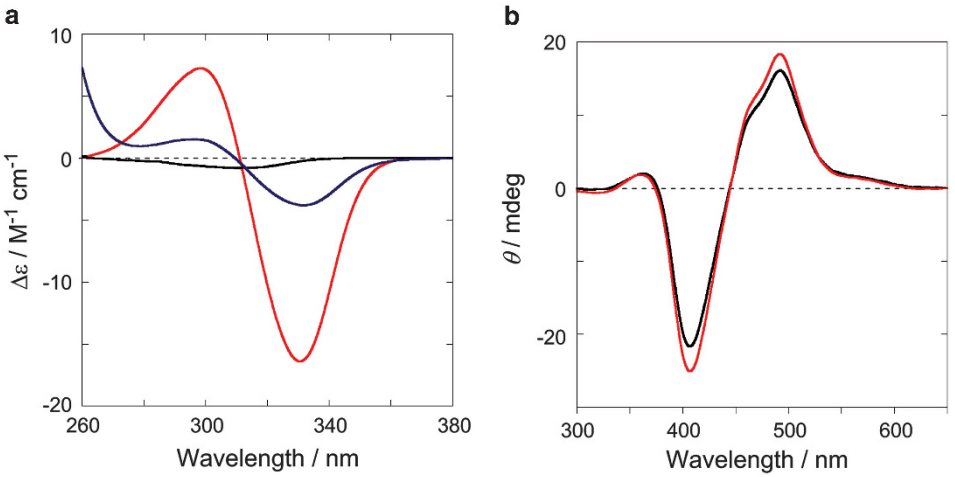


Figure 3 (**a**) CD spectra of DABz-Cur in DMSO (0.341 mM in monomer unit; black) and in 1:9 (v/v) DMSO-H_2O (0.462 mM in a monomer unit) in the absence (red) and presence (blue) of acarbose (30 mM) at 25 °C (original data from Fukura and Inoue[26]). (**b**) CD spectra of a 1:9 (v/v) DMSO-H_2O solution of 0.2 mM PyPT and 0.5 mM Cur (concentrations in monomer unit) in the absence (black) and presence (red) of 1 μM acarbose at 25 °C (original data from Fukura and Inoue[27]).

hypsochromic shift at longer wavelengths (450 nm), indicating that the PT backbone deforms upon complexation with a chiral guest, as illustrated in Scheme 2b. From the UV/vis spectral changes, we can easily determine the association constants (K_D or K_L) and enantioselectivities ($K_{D(D)}/K_{L(L)}$) of all the guests by Hill analysis. The CDPT sensor favors the D-amino acids and D,D-dipeptides, with the exception of His (no chiral discrimination). This selectivity was indeed the case for the aromatic D,D/L,L-dipeptides pairs examined, and much higher affinities and enantioselectivities were achieved. Particularly, D,D/L,L-Phe–Phe and Tyr–Tyr were strongly bound and much more efficiently differentiated, with enantioselectivities ($K_{D(D)}/K_{L(L)}$) of 13.7 and 8.0, respectively, in contrast to those for DD/LL-Gly-Tyr and Phe–Trp (1.1 and 3.5, respectively). This discriminating behavior indicates that the homosequence dipeptides are better differentiated than the heterosequence dipeptides. The Hill coefficients (n) obtained for the D-amino acids and D,D-dipeptides are in the 0.7–1.2 range, which suggests negative or less efficient positive cooperation, whereas those of the antipodal L(L) guests are consistently larger than unity ($n = 1.0$–1.8), which indicates positive cooperation, in particular for L-Tyr ($n = 1.8$). This result is somewhat disappointing in view of the D(D)/L(L) selectivity in terms of a trade-off relationship at least for the present CDPT sensor. Nevertheless, we have also demonstrated the expanded SASS principle in sensing a biologically important guest with the CDPT sensor in aqueous solution, achieving a remarkably high enantioselectivity of up to 13.7 for the DD/LL-Phe–Phe pair.[25]

It is therefore concluded that the SASS strategy is attractive, is potentially extendable to the chirality sensing of a wide variety of chiral guests by using a suitable sensing moiety and is thus more advantageous than those strategies employed in conventional chiroptical sensors.

CURDLAN-BASED SUPRAMOLECULAR OLIGOSACCHARIDE SENSING

Selective oligosaccharide sensing in aqueous media is one of the most intriguing but highly challenging processes in current chemistry because of the heavy hydration and stereochemical diversity of the oligosaccharides.[4,5,12] In this section, the author describes the recent reports of oligosaccharide sensing by using Cur hosts.[26,27] Cur, shown in Figure 2b, is essentially a linear glucan composed of (1 → 3)-linked β-D-glucose units and forms a triple-helical structure.[41,42] An interesting feature of the Cur helix is the reversible denaturing–renaturing process driven by solvent switching from water or acidic solution to DMSO or aqueous alkaline solution.[42–44] Sakurai, Shinkai and co-workers revealed that a polynucleotide merges with the glucan schizophyllan to form a hetero-triplex by replacing one of the three glucan components.[45,46] This phenomenon led us to use the glucan triplex as a key tool for sensing only the saccharides that nicely splice into the triple-helical hydrogen-bonding network of the glucan.

To thus construct a Cur-based saccharide sensor operative in aqueous media, we synthesized the reporter-modified Cur, 6-*O*-(4-dimethylamino)benzoyl) Cur (DABz-Cur; Figure 2a) and used CD spectroscopy to investigate its ability for sensing a variety of saccharides. DABz-Cur was prepared in 92% yield by the reaction of DABz chloride with native Cur, which was swollen overnight in

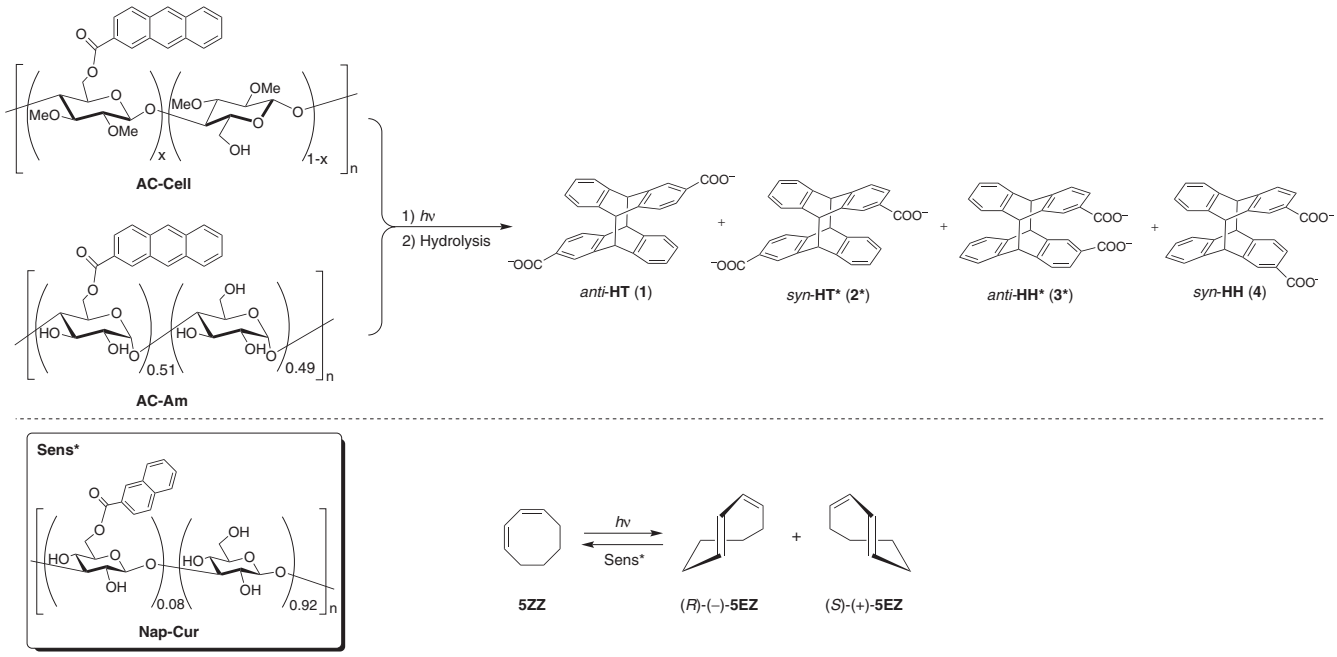


Figure 4 (upper panel) Diastereodifferentiating photocyclodimerization of 2-anthracencecarboxylate tethered to cellulose (AC-Cell) and amylose (AC-Am) scaffolds. (lower panel) Enantiodifferentiating photoisomerization of (*Z*,*Z*)-1,3-cyclooctadiene included and sensitized by naphthoyl-Cur (Nap-Cur).

N-methyl-2-pyrrolidinone at 100 °C before the reaction. The degree of substitution of the DABz-Cur thus obtained was determined as 0.12 from the ^{1}H NMR spectrum. The CD spectrum of DABz-Cur measured in DMSO showed an extremely weak negative Cotton effect at the charge-transfer band of DABz centered at 310 nm (the black line in Figure 3a), indicating that the Cur is disassembled to a single strand. In sharp contrast, an intense negative exciton couplet was observed at the same charge-transfer band in 1:9 (v/v) DMSO-H_2O (the red line in Figure 3a), suggesting a left-handed helical arrangement of the DABz chromophores. However, the superstructure in 10% DMSO aqueous solution is still under investigation and is debatable (triplex or other structure). Acarbose, shown in Figure 2a, is a drug for the treatment of type-2 diabetes mellitus and obesity, and therefore, its detection is particularly significant from a diagnostic view point.[47] Acarbose (30 mM) added to a 10% DMSO aqueous solution of DABz-Cur caused a significant reduction of the CD intensity without the couplet pattern (the blue line in Figure 3a), indicating strong interactions between acarbose and DABz-Cur in the 24 mono- to tetrasaccharides examined in this study. It is therefore noted that this strategy employing a glucan as a saccharide-sensing device and the appended chromophore as a reporter may be expandable to other analytes that are difficult to sense in aqueous media.[26]

To further demonstrate the highly selective and sensitive oligosaccharide sensing, the SASS strategy was applied to oligosaccharide sensing. We therefore chose native Cur as the hydrogen-bonding receptor for the saccharides and a water-soluble PT, 2,5-poly(3-(1-pyridinium)hexylthiophene (PyPT; Figure 2b), as a signal-amplifying reporter because Shinkai and co-workers found that schizophyllan forms stable complexes with water-soluble PTs to give helical triplexes that exhibit strong exciton couplings.[48,49] The Cur-PyPT hybrid exhibits intense positive exciton couplings at the π–π^* transition of the PT main chain (the black line in Figure 3b), indicating the formation of a stable Cur-PyPT hetero-triplex with a right-helical PT backbone. We investigated the selectivity of the Cur-PyPT hybrid sensor upon complexation with 24 mono- to pentasaccharides, and all 24 examined saccharides more or less augmented the ellipticity, indicating that the PT helix is further twisted by the incorporation of the saccharide into the Cur-PyPT complex. Intriguingly, among the examined saccharides, acarbose was most effective in enhancing the ellipticity (the red line in Figure 3b). It is noted that the SASS strategy is also effective for oligosaccharide sensing in aqueous media and is hence capable of sensing at low detection limits (1 μM) with high selectivity.[27]

POLYSACCHARIDE-BASED CHIRAL PHOTOCHEMISTRY

In this section, we have expanded ground-state supramolecular sensing to excited-state chiral photochemistry by using the polymers mentioned above, and hence the author reports recent examples of polysaccharide-based photochirogeneses,[34–36] which is still a challenging topic in current chiral photochemistry.[28–33]

First, we chose the photocyclodimerization of 2-anthracencecarboxylate (AC) as a model photochirogenic reaction, which gave four stereoisomers upon photoirradiation, that is, anti-head-to-tail (**1**), syn-head-to-tail (**2***), anti-head-to-head (**3***) and syn-head-to-head cyclodimers (**4**), two of which are chiral (**2*** and **3***);[50] 2,3-di-*O*-methylcellulose is a chiral flexible polymer backbone, as shown in Figure 4 (top). Thus, we synthesized a series of AC-appended methylcellulose compounds (AC-Cells) of varying degree of substitution (0.22, 0.42 and 0.53) and examined their chiroptical properties. Then, the AC-Cells were subjected to diastereodifferentiating photocyclodimerization under a variety of conditions. The chiroptical properties of AC-Cell$_{42}$ were examined in DCM, and a relatively weak negative exciton couplet with an amplitude of $\Delta\varepsilon = 9.5\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$ at the major ^1B_b band was observed, indicating a left-handed helical conformation on average that is probably due to the flexible methylcellulose scaffold. Photoirradiation of AC-Cell$_{42}$, followed by saponification, gave the favored HH dimers (**3*** and **4**) with an average HH/HT ratio of 67:33 with 18% enantiomeric excess (e.e.) of **2*** and 22% ee of **3*** at 60 min irradiation. Interestingly, the product distribution (HH/HT ratio) and e.e. obtained in the

photocyclodimerization of the AC-Cells are very dependent on the irradiation period and the degree of substitution. The HH/HT ratio and e.e. of **2*** were larger for shorter irradiation periods (<1 min irradiations) and afforded the best values of 90:10 and 20%, respectively, while the e.e. of **3*** increased from 7 to 18% upon extending the irradiation time from 15 s to 62 min. Combined with kinetic analyses, an intrachain cross-linking photocyclodimerization occurs in the initial stage, and then, the gradually decreasing mobility of the polymer chain effectively discourages the photocyclodimerization of the HH-oriented AC pairs at more distant positions in the later stage. By using a flexible polymer scaffold, we have therefore demonstrated that intramolecular cross-linking photocyclodimerization has a decisive role in controlling the HH/HT ratio as well as the e.e. of the chiral products.[34]

Next, we employed the inherently helical amylose, which is known to form left-handed single helices in DMSO or aqueous DMSO solution, as a chiral scaffold in the same photochirogenic AC reaction and thus synthesized AC-appended amylose (AC-Am), as shown in Figure 4 (middle). The chiroptical properties of AC-Am were examined in DMSO-H_2O, and the CD spectra of AC-Am showed sharp negative exciton couplets with an amplitude of $\Delta\varepsilon = \sim 45\,M^{-1}\,cm^{-1}$ at the ^1B_b band in 100 and 75% DMSO solutions and broader, blue-shifted negative couplets with an amplitude of $\Delta\varepsilon = \sim 28\,M^{-1}\,cm^{-1}$ in 50–10% DMSO solutions, indicating that the AC chromophores of AC-Am align homogeneously along the helical amylose backbone in DMSO but become less ordered in water-rich DMSO solutions. Photoirradiation (<3 min) of AC-Am at 25 °C followed by saponification gave 71% HH selectivity and an e.e. (**2***) of 12% in DMSO but a discouraging 65% HH selectivity and an e.e. (**2***) of 13% in 10% DMSO aqueous solution. Interestingly, the addition of γ-cyclodextrin as a second chiral source affects the product distribution and the e.e., thus dramatically changing the favored HH selectivity to HT selectivity (76%) with higher e.e. (**2***) of 37% at −15 °C. We have therefore demonstrated that dual chiral and supramolecular photochirogenesis was successfully applied to polysaccharide-based chiral photochemistry by using amylose as a chiral scaffold and γ-cyclodextrin as a chiral host.[35]

Finally, we have expanded the polymer-based diastereodifferentiating photochirogenesis to the more difficult enantiodifferentiating photoreaction. We have employed a sensitizer-appended Cur, 6-*O*-(2-naphthoyl)curdlan (Nap-Cur), as a sensitizing host and investigated the enantiodifferentiating photoisomerization of (*Z*,*Z*)-1,3-cyclooctadiene (**5ZZ**),[51] which was included and sensitized by Nap-Cur, as shown in Figure 4 (bottom). In 10% aqueous DMSO solution, Nap-Cur showed a negative Cotton effect at the ^1B_b band, as is the case with DABz-Cur, and the addition of **5ZZ** to the solution containing Nap-Cur caused reduced couplet amplitude of the ^1B_b band of Nap-Cur because of the conformational changes. Upon irradiation in DMSO, in which Nap-Cur forms a random coil, almost racemic **5EZ** (0.7% e.e.) was obtained, whereas **5EZ** was produced with a much better e.e. of 8.7% in 3:7 DMSO-H_2O at 25 °C. Interestingly, the inclusion complex of **5ZZ** with Nap-Cur prepared as precipitate gave the highest e.e. of 11.7% upon photoirradiation at −160 °C. It is therefore noted that the polysaccharide-based chiral photochemistry was successfully expanded to the more difficult enantiodifferentiating photochirogenesis.[36]

CONCLUSIONS

The author has proposed an 'SASS' methodology and has further demonstrated the usefulness of the SASS principle in PT- and curdlan-based chirality or oligosaccharide sensing. The successful SASS behaviors are responsible not only for the amplification of the signal but also for allosteric, flexible polymer backbones and hence may be expandable to other amplifying polymers with appropriate complementary functional groups. The author therefore believes that the results and concepts presented in this review are scientifically stimulating and practically useful for those working in macromolecular, supramolecular and photochemistry.

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