Novel saccharide tweezers with a diarylethene photoswitch

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A photochromic saccharide receptor with a diarylethene photoswitch changes the binding event with glucose by photoirradiation.

Switching of host–guest events by photoirradiation has been investigated vigorously by use of a variety of photochromic compounds,[1] since it enables us to carry out active transport of guest molecules and to use them as guest launchers by photoirradiation. Recently, boronic acids have been extensively used for recognition of saccharides with important roles in biological systems.[2] However, to the best of our knowledge, there has been no report on a photoswitchable saccharide receptor. Here we show the first example of photochromic saccharide tweezers[1a,3] with a diarylethene unit as a switch. Among the various types of photochromic compounds, diarylethenes with heteroaromatic rings have favourable properties for the photoswitch unit, especially their fatigue resistance and thermally irreversible properties.[4]

Fig. 1 shows the concept of this photochromic saccharide receptor.

The open-ring form has two conformers, anti-parallel and parallel. These conformers exchange rapidly at room temperature and only the anti-parallel conformer undergoes photoisomerization to give the closed-ring form by irradiation with UV light.[5] In the parallel conformer, two binding sites face each other like tweezers. Saccharides have many hydroxy groups

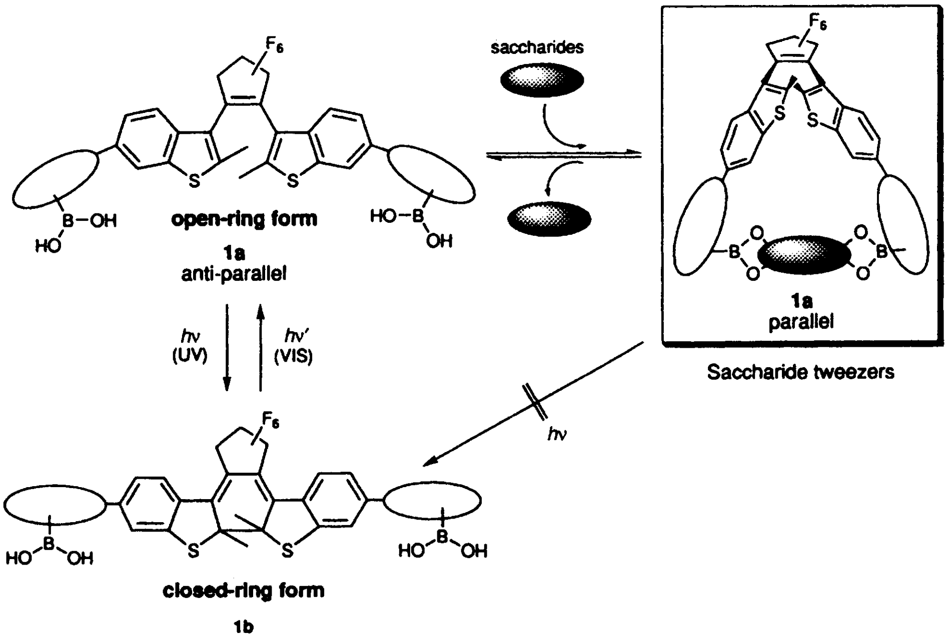
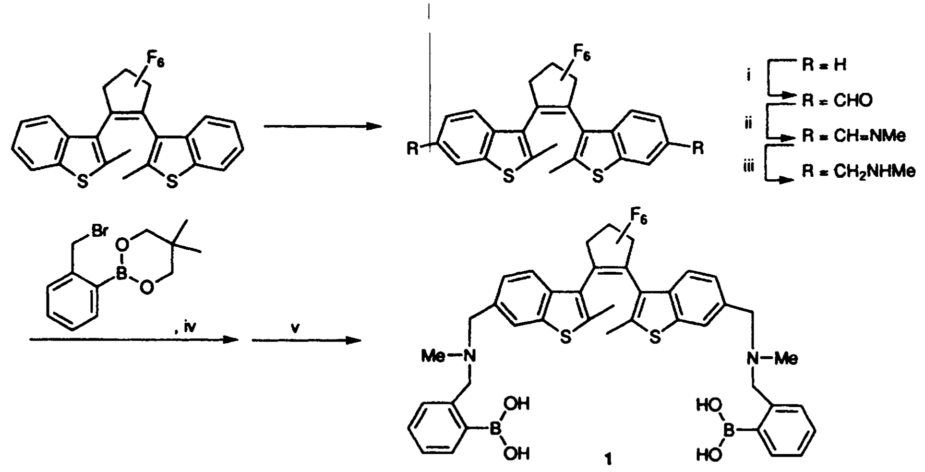


Fig. 1 Concept of photoswitchable molecular tweezers having a diarylethene group



Scheme 1 *Reagent and conditions*: i, Cl_2CHOMe, $AlCl_3$, $PhNO_2$, 57%; ii, $MeNH_2$, MeOH, quant.; iii, $NaBH_4$, MeOH, quant.; iv, K_2CO_3, MeCN, 60%; v, Na_2CO_3, MeOH, water, quant.

which can form esters with boronic acids, therefore one can expect the parallel conformer to form a 1 : 1 complex with saccharides because two faced boronic acids can form boronate linkages with four hydroxy groups. On the other hand, in the closed-ring form the boronic acid groups are separated and cannot form the complex.

The photoswitchable receptor **1**‡ was synthesized from 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene as shown in Scheme 1.[5]

Receptor **1a** has an absorption maximum at 229 nm ($\varepsilon = 5.4 \times 10^4$ M^{-1} cm^{-1}) in EtOH–Tris–HCl buffer (pH 7.8) (1 : 1). Upon irradiation with 313 nm light, the open-ring form **1a** converted to the closed-ring form **1b** with an absorption maximum at 533 nm in 60% yield, determined by the spectrum of the isolated **1b** ($\varepsilon = 8.3 \times 10^3$ M^{-1} cm^{-1}) in the photostationary state (PSS). The pink colour disappeared upon irradiation with visible light ($\lambda > 480$ nm) and the absorption spectrum was the same as before irradiation. The receptor **1** is achiral and absorbs UV light, whereas saccharides are chiral and do not absorb UV light. The complex of **1** and saccharide is chiral and absorbs UV light. Therefore one can expect that the complex is circular dichromism (CD) active.[6] Fig. 2 shows a CD spectra change of 100% **1a** (1.4×10^{-5} M^{-1}) in EtOH–Tris–HCl buffer (pH 7.8) (1 : 1) upon addition of D-glucose. The $\Delta\varepsilon$ at 224 nm increases when D-glucose is added. The concentration dependence of the CD spectra is shown in Fig. 3.

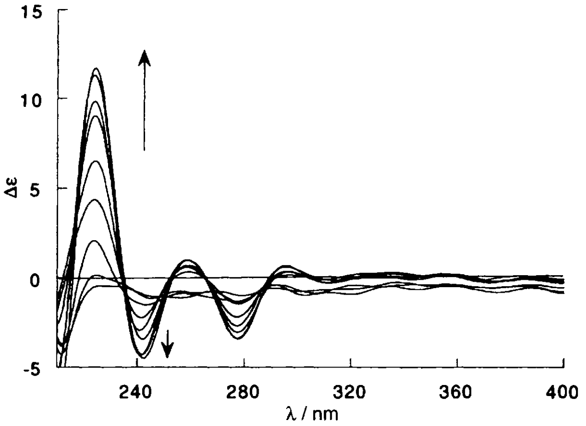


Fig. 2 CD spectra change upon addition of D-glucose {[**1a**] = 1.4×10^{-5} M, [D-glucose] = 0–7 $\times 10^{-3}$ M in EtOH–Tris–HCl buffer (pH 7.80) (1 : 1)}

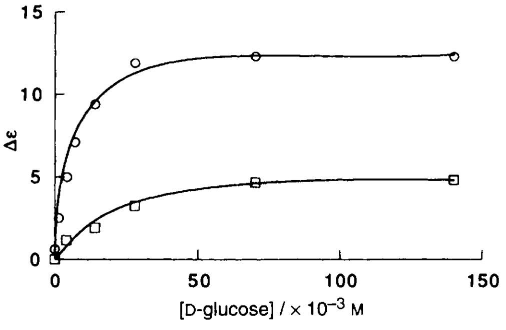


Fig. 3 [D-glucose] *vs.* $\Delta\varepsilon$ at 224 nm [circle, 100% **1a**; cube, PSS at 313 nm (**1a**: **1b** = 4/6)]

The Benesi–Hildebrand plots[7] shows good linearity, therefore the complex that is CD active can be assigned as a 1 : 1 complex. The lack of photochromic reactivity of **1** in the presence of glucose also supports the formation of a 'tweezer' type 1 : 1 complex.[8]

When **1** was irradiated with 313 nm light, the saturated $\Delta\varepsilon$ value of the PSS$_{313}$ decreased to 40% of that of the 100% open-form. From the Benesi–Hildebrand plot, stability constants (*K*) were obtained. The *K* value of 100% **1a** with D-glucose was 171 (M^{-1}), whereas that of the PSS$_{313}$ with D-glucose was 68 (M^{-1}). The *K* value of **1** at the PSS$_{313}$ with glucose is 40% of that of 100% **1a**. These results indicate that the number of host molecules which are CD active by complexation with glucose was decreased to 40% upon irradiation with 313 nm light. Irradiation of **1** at the PSS$_{313}$ in the presence of D-glucose (7.0×10^{-2} M) with visible light changes the $\Delta\varepsilon$ value from 4.8 to 12, which is the same as that of the 100% open-form, indicating that the complexation ability was fully restored. This result shows that photoreversible switching of the binding event functions in this system.

Footnotes

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‡ *Spectral data* for **1a** (100% open-form): ^{1}H NMR (200 MHz, 20 °C, in CD$_3$OD): δ 2.21 (2.4 H, s, ap), 2.35 (3.6 H, s, p), 2.37 (2.4 H, s, ap), 2.56 (3.6 H, s, p), 3.90 (0.8 H, s, ap), 3.95 (0.8 H, s, ap), 4.04 (4.8 H, s, p), 4.15 (1.6 H, s, p), 7.05–7.31 (8 H, m), 7.52–7.93 (8 H, m); Although the ^{1}H NMR spectrum shows parallel (p) and anti-parallel (ap) conformers of **1a** separately, these conformers exchange at a slower rate than the NMR timescale and could not be separated at room temperature. MS (SIMS positive): 935 [M + (glycerol − 2H$_2$O) + H]$^+$.

References

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