Enhancement of the photocyclization quantum yield of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]-thiophene-6-sulfonate) by inclusion in a cyclodextrin cavity

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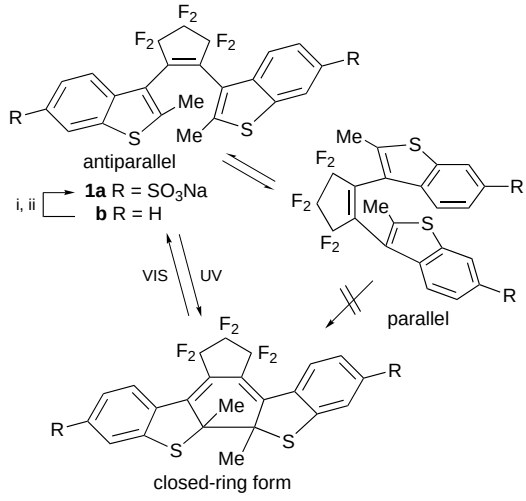
The photocyclization quantum yield of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) is found to increase in aqueous solution after the addition of β- and γ-cyclodextrin, in which a photoreactive antiparallel conformation of diarylethene is favourably included.

Photochromic reaction of diarylethenes are based on reversible photocyclization of hexatriene structures, as shown in Scheme 1.[1] The opened ring form of diarylethene has two conformations, parallel and antiparallel. The photocyclization can proceed only from the antiparallel conformation, while the parallel conformation is photochemically inactive.[2] The conformational change between the antiparallel and parallel conformations in solution limits the maximum cyclization quantum yield to 0.5.[3] If one can increase the ratio of antiparallel : parallel conformation, the cyclization quantum yield is expected to increase accordingly.

It is well known that cyclodextrins (CDs) have cavities whose sizes are dependent on the number of glucopyranose units, and can include various types of organic compounds by hydrophobic interactions in aqueous media.[4] Here we have attempted to control the ratio of the two conformations in an aqueous solution by including the 3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophene-6-sulfonate) in the CD cavities.

2,2′-Dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis-(benzo(*b*]thiophene-6-sulfonate)‡ **1a** was prepared by treatment of 2,2′-dimethyl-3,3′-(perfluorocyclopentene-1,2-diyl)bis(benzo[*b*]thiophen)[5] **1b** with chlorosulfonic acid in $CHCl_3$ and subsequent hydrolysis with 1% aqueous NaOH (Scheme 1).

Fig. 1(*a*) shows the ^{1}H NMR spectrum of the methyl groups of the open-ring form of **1a** in D_2O (3.0×10^{-3} mol dm^{-3}, 20 °C, 200 MHz). The methyl signals of each conformation are



Scheme 1 *Reagent and conditions*: i, $ClSO_3H$, $CHCl_3$, room temp.; ii, 1% NaOH, 78%

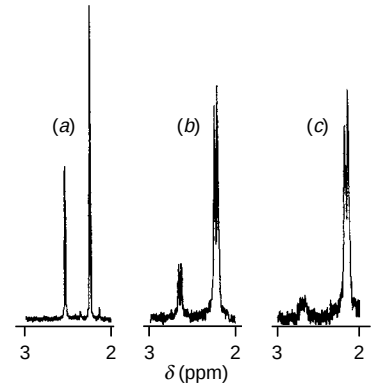


Fig. 1 ^{1}H NMR spectra of methyl protons in D_2O ([**1**] = 3.0×10^{-3} mol dm^{-3}); (*a*) **1a**, (*b*) **1a**–β-CD (1 : 5) and (*c*) **1a**–β-CD (1 : 10)

observed separately. This indicates that the conformational change takes place slowly relative to the NMR timescale (< 56 Hz). The methyl protons at δ 2.27 (at higher magnetic field) are assigned to the antiparallel conformation.[2] Under the present conditions, the antiparallel conformation is favoured and the ratio of antiparallel : parallel was 64 : 36. This value shows that only 64% of **1a** is photoreactive. Upon addition of β- and γ-CD to this solution, the ratio of antiparallel : parallel conformations was increased, as shown in Fig. 2. When 10 equiv. of β-CD were added to the solution, the antiparallel conformation became dominant, as shown in Fig. 1(*c*). On the other hand, the addition of α-CD did not change the ^{1}H NMR spectrum of **1a**. These results reveal that the cavity of β-CD is suitable for the antiparallel conformation of **1a**, whereas that of α-CD is too small to include **1a**. γ-CD is considered to have a small association constant with the diarylethene. The splitting of each

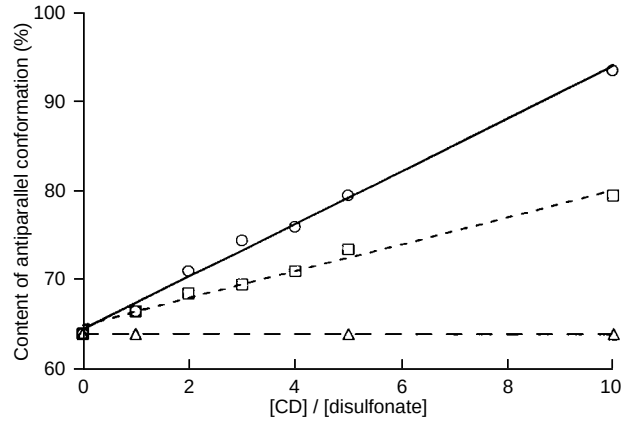


Fig. 2 [CD]/[**1a**] *vs.* content of antiparallel conformation determined by ^{1}H NMR spectroscopy ([**1a**] - 3.0×10^{-3} mol dm^{-3}); (△) with α-CD, (○) with β-CD and (□) with γ-CD

Table 1 Cyclization quantum yields of **1a** irradiated with 313 nm light in the presence of CD in aqueous solution[a]

System	**1a**	**1a**–α-CD	**1a**–β-CD	**1a**–γ-CD
Quantum yield	0.38	0.37	0.58	0.53

[a] [**1a**] = 4.0×10^{-5} mol dm^{-3}; [CD] = 8.0×10^{-3} mol dm^{-3}, 20 °C.

methyl proton of the both conformations of **1a** was observed in β-CD. The split suggests that the two methyl protons exist in different environments in the chiral CD cavity.

As described above, the diarylethene in the parallel conformation is not photoreactive. Therefore, the increase in the ratio of antiparallel : parallel conformations is expected to result in an increase in the cyclization quantum yield. Table 1 shows the cyclization quantum yields of **1a** irradiated with 313 nm light.[3,6]

As expected, the cyclization quantum yield of **1a** in the presence of a 200-fold excess of β-CD is *ca.* 1.5 times larger than that of **1a** in aqueous solution. NMR measurements indicated that almost all the diarylethene is in the antiparallel conformation in the presence of excess β-CD. The increase in the quantum yield is due to the increase in the proportion of molecules in the antiparallel conformation. On the other hand, no change was observed in either the ^{1}H NMR spectrum or the quantum yield for cyclization of **1a** in the presence/absence of α-CD. The enhancement of quantum yield in the presence of β- and γ-CD is ascribed to the favourable antiparallel conformation of **1a** in the CD's cavities.

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Footnotes and References

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‡ *Selected data* for **1a** (100% open form): δ_H (200 MHz, 20 °C, D_2O) 2.27 (3.84 H, s, ap), 2.55 (2.16 H, s, p), 7.58–7.96 (4 H, m, ap and p), 8.14 (0.72 H, s, p), 8.26 (1.28 H, s, ap) [although the spectrum shows parallel (p) and antiparallel (ap) conformers separately, these conformers exchange slowly relative to the NMR timescale]; Calc. for $C_{23}H_{12}F_6O_6S_4Na_2 \cdot H_2O$: C, 40.00; H, 2.04. Found: C, 39.56; H, 2.27%; λ_{max}/nm (ε) open-ring form: 233 (49 000), closed-ring form: 529 (9800); MS(FAB+) *m*/*z* 673 $[M + 1]^+$.

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