Enantiodifferentiating photocyclodimerization of cyclohexa-1,3-diene sensitized by chiral arenecarboxylates

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The enantiodifferentiating photosensitized cyclodimerization of cyclohexa-1,3-diene **1** was performed over a range of temperatures in the presence of chiral arene(poly)carboxylates, giving *endo-* and *exo-*[4 + 2] cyclodimers (**2a**, **2b**) and *anti-* and *syn-*[2 + 2] cyclodimers (**3a**, **3b**). Among the three chiral cyclodimers (**2a**, **2b**, **3a**), only **2b** was obtained as an optically active species with an enantiomeric excess (ee) of up to 8.2%. The detailed reaction mechanism and the origin of the enantiodifferentiation have been elucidated, and the crucial role played by the 'microenvironmental polarity' around the chromophore in determining the photoreactivity and the ee of the product is also discussed.
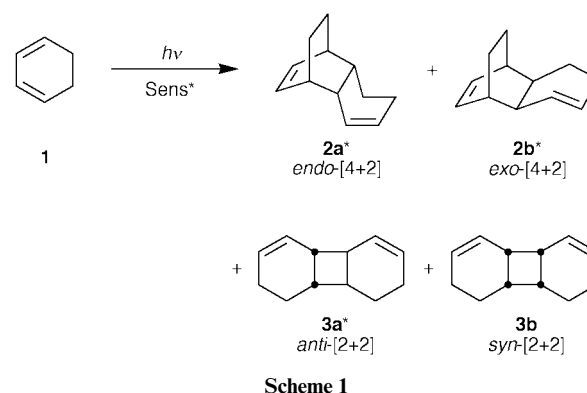
Enantiodifferentiating photosensitization, which necessitates only a catalytic amount of chiral sensitizer, is one of the most promising methodologies for inducing chirality into prochiral substrates through the electronically excited state.[1] Since the first report on the asymmetric photosensitization of *trans*-1,2-diphenylcyclopropane by Hammond and Cole,[2] a great deal of effort has been devoted to the study of enantiodifferentiating photosensitized isomerizations, but the reported enantiomeric excesses (ee's) have rarely exceeded 10%, until recently.[2–12,20h] We have demonstrated that the enantiodifferentiating geometrical photoisomerization of (*Z*)-cyclooctene, sensitized by chiral benzenepolycarboxylates gives the optically active (*E*)-isomer in exceptionally high ee's of up to 64% at −89 °C, and displays the interesting property of product chirality inversion, induced by temperature and pressure changes.[5b,h,k]

In contrast to the unimolecular enantiodifferentiating photoisomerizations, only a few attempts have been reported on bimolecular enantiodifferentiating reactions. The enantiodifferentiating [2 + 2] photocyclodimerizations of aryl vinyl ether and 4-methoxystyrene in acetonitrile were examined in the presence of some chiral naphthalenecarboxylates to give the corresponding cyclodimers in good chemical yields, but no enantiodifferentiation occurred (ee < 1%).[13] Kim and Schuster reported that the [4 + 2] photocycloaddition of *trans*-β-methylstyrene with cyclohexa-1,3-diene sensitized by (−)-1,1′-bis(2,4-dicyanonaphthalene), gave the cyclodimer with 15% ee at −65 °C.[14f]

Recently we reported that the enantiodifferentiating photoaddition of alcohols to 1,1-diphenylalkenes sensitized by chiral naphthalene(di)carboxylates gives the anti-Markovnikov adduct.[15] In this bimolecular asymmetric photosensitization, we observed an unusual temperature effect on the enantioselectivity of the product. It was found that the product chirality was inverted by temperature at the critical point (T_0), which enabled us to obtain both of the enantiomeric products simply by changing the irradiation temperature, also allowing higher ee's to be obtained at higher temperatures beyond T_0.[15] We have also found that the chemical and optical yields of the product are critically controlled by the 'microenvironmental polarity' around the sensitizer chromophore, showing that the introduction of saccharide substituent(s) to the sensitizer works as a new effective strategy for overcoming the trade-off between the chemical and optical yields in such photoaddition reactions involving a radical ion intermediate. By combining the unusual temperature effect and the enhanced microenvironmental polarity by introducing saccharide substituent(s) to the sensitizer, we obtained the optimized ee of 33%.[15]

Photocycloaddition initiated by energy or electron transfer is one of the most widely investigated photochemical reactions.[16] The photocycloadditions of 1,3-dienes to arenes have been used in the syntheses of various types of novel cyclic compounds.[14e,17–20] The photocyclodimerization of cyclohexa-1,3-diene (**1**) which gives isomeric [4 + 2] and [2 + 2] cyclodimers (**2** and **3**) (Scheme 1) has also been investigated under a variety

Scheme 1

of conditions, for which several reaction mechanisms involving different intermediates have been proposed, depending on the mode of excitation.[14b,20–22] Here, we report the result of our study of the enantiodifferentiating photocyclodimerization of **1** sensitized by chiral arene(poly)carboxylates. The use of chiral sensitizers with saccharide and non-saccharide substituents has enabled us to obtain definitive evidence for the cyclodimerization mechanism. Furthermore, it has allowed exploration into the enhancement of the microenvironmental polarity to increase the chemical yield without decreasing the ee of the product, by preventing the dissociation of the photochemically generated radical ion pair.

Results and discussion

Photocyclodimerization of cyclohexa-1,3-diene (1)

The [4 + 2] and [2 + 2] cyclodimerizations of **1** have been

investigated under a wide variety of thermal and photo-chemical conditions.[14b,20–25] The thermal dimerization requires a long reaction time and affords the *endo*- and *exo*-Diels–Alder adducts **2a** and **2b** in poor yields, with an *endo*:*exo* ratio of *ca.* 4:1.[21a,25] However, photochemical reactions of **1** lead to the formation of both [4 + 2] and [2 + 2] cyclodimers. Direct irradiation of neat **1** at 254 nm produces the *exo*-[4 + 2] adduct **2b** and the *anti*- and *syn*-[2 + 2] adducts **3a** and **3b** in 1:4.4:2.3 ratio together with other dimers,[22] whereas photosensitization with a triplet sensitizer such as phenanthrene and benzo-phenone gives the same products **2b**, **3a** and **3b** but in higher combined yields. The relative product ratio (**2b**:**3a**:**3b** = *ca.* 1:3:1) is appreciably different from that obtained in the direct excitation and is independent of the triplet energy and structure of the sensitizer employed.[20h] In contrast, the photoinduced electron-transfer reaction of **1** leads to the *endo*-adduct **2a** in improved yield and selectivity.[20e,h] We performed the electron-transfer and triplet-sensitized photocyclodimerization of **1**, using 1-cyanonaphthalene (1-CN) and benzophenone (BP). As can be seen from Table 1 (runs 1 and 2), the photoinduced electron-transfer with 1-CN gave **2a** as the major product along with much smaller amounts of **2b**, **3a** and **3b** in a ratio of 27.8:4.2:3.0:1.0. The triplet sensitization with BP gave only **2b**, **3a** and **3b** in a ratio of 0.8:3.0:0.8, which is in good agree-ment with the results reported by Mattay *et al.*[20h]

In the present study, we have employed a variety of optically active (poly)alkyl benzene- and naphthalene(poly)carboxylates (**4**–**12**) as chiral sensitizers for the enantiodifferentiating photo-cycloaddition of cyclohexa-1,3-diene **1**, as illustrated in Chart 1. Although arene(poly)carboxylates have not frequently been used as sensitizers in photoinduced electron transfer reactions,[26,27] they are prominent and effective chiral sensitizers[15b,c] for the enantiodifferentiating photoaddition, which will allow us to examine a wide variety of chiral auxiliar-ies introduced into the vicinity of the chromophore.

In performing optically and chemically efficient enantio-differentiation in a photoreaction that involves an electron transfer process and radical ionic species, one of the most important factors is the choice of solvent. In general, the use of a polar solvent is an essential condition for high chemical yield, which however often accompanies a decreased optical yield of photoproduct as a result of the intervention of free or solvent-separated radical ion pairs between the chiral sensitizer and substrate.[5i,14f,15] We have therefore employed nonpolar or less polar solvents in the present enantiodifferentiating photocyclo-dimerization of **1**.

Arenecarboxylate sensitizers

In search of the most effective arenecarboxylate sensitizers for the photocyclodimerization of **1**, benzenepolycarboxylates (**4** and **5**) and naphthalene(poly)carboxylates (**6**–**12**) with several chiral auxiliaries (**a**–**f**) (shown in Chart 1) were examined. Using optically active arenecarboxylates (5 mmol dm^{-3}), the photo-sensitized cyclodimerization of **1** (100 mmol dm^{-3}) was per-formed in either pentane, toluene, diethyl ether or acetonitrile at −41 and + 25 °C to give **2a**, **2b**, **3a** and/or **3b**. Of these four cyclodimers, **2a**, **2b** and **3a** are chiral, as indicated by an asterisk in Scheme 1. The chemical yields and the enantiomeric excesses (ee's), as determined by chiral stationary-phase gas chromato-graphy, are summarized in Table 1. Since the enantiomers of the cyclodimers could not be isolated on a preparative scale, the sign of the reported ee value is just a tentative one representing the order of elution from the Supelco β-Dex 120 and 325 columns, and therefore may not coincide with the direction of the optical rotation of the product. Thus, a positive value means the predominant formation of the first-eluted enantiomer.

The photocyclodimerizations sensitized by chiral arene-(poly)carboxylates possessing (−)-menthyl and (−)-8-phenyl-
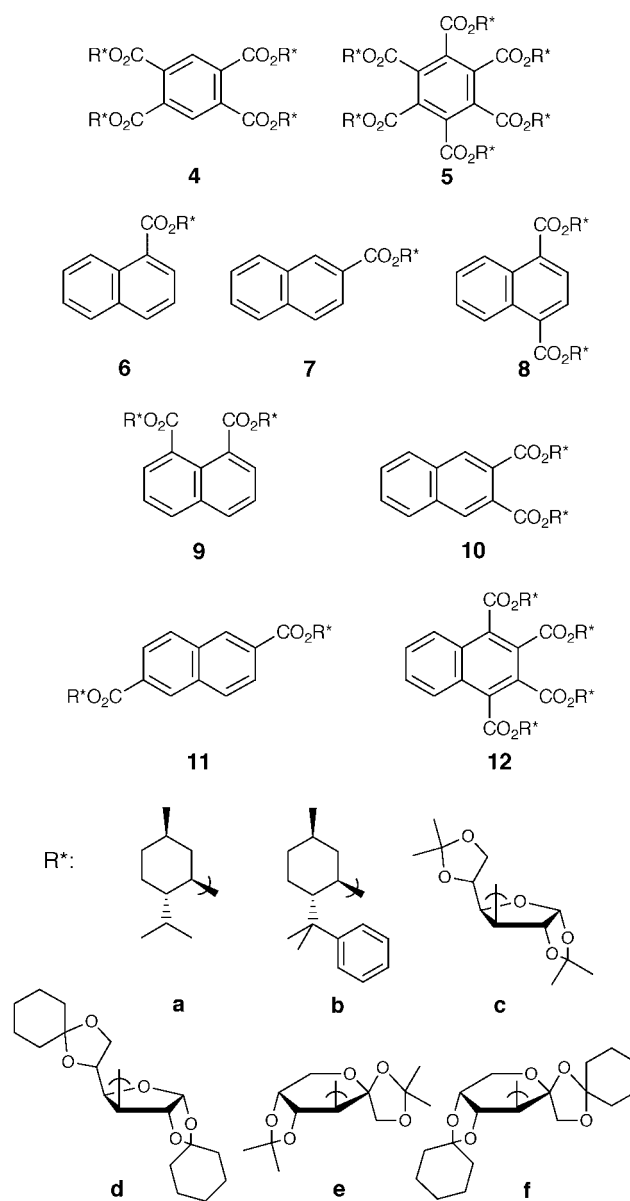
Chiral Sensitizers

Chart 1

menthyl auxiliaries were performed in pentane and toluene at 25 and −41 °C. Polymenthyl benzenepolycarboxylates which were used as singlet energy-transfer sensitizers for photo-isomerization of cycloalkenes[5] were examined first. As can be seen from Table 1, the singlet sensitization with benzene-tetracarboxylate **4a** (runs 3–6) and benzenehexacarboxylate **5a** (runs 7–10) gave cyclodimers **2b**, **3a** and **3b** in low chemical yields but never produced the *endo*-dimer **2a**. Irrespective of the solvent and sensitizer used, effectively the same product ratio was obtained at 25 °C, *i.e.* **2b**:**3a**:**3b** = 1.2:3.0:1.0, which is slightly different from that observed for triplet sensitization with BP, *i.e.* **2b**:**3a**:**3b** = 0.8:3.0:0.8. However, the product dis-tribution was affected by the irradiation temperature, with the ratio of **3b** decreasing at lower temperatures, while the **2b**:**3a** ratio stayed constant. The ee of **2b** was generally low (<2.5%) at 25 °C but was appreciably enhanced to 4.0% in toluene at −41 °C, upon sensitization with **5a**. Conversely, low ee's (<2%) were obtained for **3a** at 25 °C and were not improved even at −41 °C.

We further examined chiral naphthalene(poly)carboxylates, which are often used in photoinduced electron-transfer reactions.[15] Photosensitized cyclodimerization of **1** using naphthalenecarboxylates **6a** and **7a** (runs 11-14 and 19–22,

Table 1 Enantiodifferentiating photocyclodimerization of **1** sensitized by 1-cyanonaphthalene (1-CN), benzophenone (BP) and chiral arene(poly)-carboxylates **4–12** [a]

Entry	Sensitizer	Solvent	Temperature/°C	Irradiation time/h	Conversion (%)	2a	2b	3a	3b
						% yield (% ee [b])			
1	1-CN	Acetonitrile	25	6	61	21.3 (−0.1)	3.2 (−0.3)	2.3 (−0.3)	0.8
2	BP	Acetonitrile	25	6	>99	0	8.7 (+0.2)	30.9 (+1.0)	8.4
3	**4a**	Pentane	25	2	44	0	2.3 (+2.5)	6.0 (−0.9)	1.9
4			−43	4	49	0	1.3 (+2.8)	3.4 (−1.5)	0.8
5		Toluene	25	2	56	0	1.7 (−0.6)	4.3 (−1.0)	1.7
6			−41	4	22	0	1.1 (+0.3)	2.6 (−0.7)	0.6
7	**5a**	Pentane	25	2	16	0	1.6 (+0.7)	3.6 (−0.8)	1.4
8			−41	4	17	0	2.0 (−0.1)	5.2 (−1.8)	1.1
9		Toluene	25	2	23	0	1.0 (+2.5)	2.5 (−1.1)	0.4
10			−41	4	13	0	1.1 (+4.0)	2.6 (−1.1)	0.6
11	**6a**	Pentane	25	2	40	0	1.7 (−0.8)	4.5 (−2.0)	1.4
12			−41	4	41	0	0.6 (−0.3)	1.7 (−1.8)	0.4
13		Toluene	25	2	21	0	1.3 (−0.1)	3.4 (−2.5)	1.1
14			−41	4	c	0	1.2 (+0.7)	3.1 (−1.5)	0.8
15	**6b**	Toluene	25	2	30	0	5.1 (−0.5)	13.2 (−0.6)	4.6
16			−41	4	24	0	2.8 (−0.2)	7.4 (−0.6)	1.5
17	**6c**	Toluene	25	2	34	0	1.7 (+0.2)	4.3 (+0.7)	1.5
18			−41	4	35	0	1.0 (−0.2)	2.5 (+0.8)	0.6
19	**7a**	Pentane	25	2	10	0	0.2 (+1.0)	0.6 (−1.6)	0.2
20			−34	4	49	0	0.1 (c)	0.3 (−0.9)	0.1
21		Toluene	25	2	11	0	<0.1 (c)	0.8 (+0.3)	<0.1
22			−41	4	10	0	0.6 (+0.5)	1.5 (0.0)	<0.1
23	**7b**	Toluene	25	2	36	0	0.6 (−0.8)	1.7 (+0.6)	0.6
24			−41	4	29	0	0.8 (−0.1)	2.2 (+0.4)	0.5
25	**7c**	Toluene	25	2	23	0	1.8 (−0.1)	4.8 (−0.2)	1.7
26			−41	4	24	0	1.8 (0.0)	4.7 (−0.1)	1.2
27	**8a**	Pentane	25	2	92	0	17.9 (0.0)	47.5 (−1.9)	15.9
28			−43	4	36	0	1.6 (+0.8)	4.0 (−1.4)	1.0
29		Toluene	27	2	76	0	15.6 (+0.1)	41.4 (−0.9)	14.0
30			−41	4	59	0	3.8 (+0.9)	10.0 (+0.1)	2.4
31		Ether	25	2	16	0	2.1 (+1.4)	5.4 (−0.3)	1.8
32			−41	4	13	0	1.5 (+0.4)	3.8 (−0.2)	0.9
33		Acetonitrile	25	2	78	26.4 (−0.1)	5.0 (+0.2)	7.8 (−1.1)	1.9
34	**8b**	Toluene	25	2	65	0	4.4 (+1.4)	11.2 (−1.4)	4.2
35			−41	4	48	0	3.5 (+3.0)	8.8 (−1.5)	2.2
36	**8c**	Pentane	25	2	51	0	7.3 (+0.4)	18.1 (−1.3)	5.4
37		Toluene	25	2	64	0.5 (c)	4.5 (−5.3)	10.8 (0.0)	4.1
38			−41	4	17	0.9 (c)	3.2 (−2.2)	7.1 (−0.6)	2.1
39		Ether	25	2	c	0.3 (c)	2.8 (−4.6)	6.3 (−0.3)	2.0
40			−41	4	c	0.5 (c)	1.3 (−6.4)	2.7 (−0.4)	0.6
41	**8d**	Toluene	25	2	21	0.4 (c)	5.3 (−2.8)	11.9 (−0.8)	4.8
42			−41	4	38	1.1 (+0.8)	3.0 (−2.0)	6.7 (−0.4)	2.0
43		Ether	25	2	c	0.3 (c)	3.1 (−2.9)	7.7 (0.0)	2.4
44			−41	4	c	0.6 (c)	2.5 (−3.6)	5.9 (−0.2)	1.3
45	**8e**	Toluene	25	2	52	0.5 (c)	3.8 (−7.6)	8.1 (−0.3)	3.1
46			−41	4	49	0.6 (c)	1.4 (−0.2)	3.2 (−0.4)	0.5
47		Ether	25	2	c	0.4 (c)	2.3 (−4.1)	4.7 (+0.3)	1.4
48			−41	4	c	0.5 (c)	1.1 (−2.5)	2.3 (−0.7)	0.6
49	**8f**	Toluene	25	2	31	0.6 (c)	5.0 (−5.1)	10.8 (−0.3)	4.2
50			25 [d]	2	42	1.3 (c)	8.8 (−2.8)	15.5 (−0.7)	5.8
51			25 [e]	2	78	4.8 (c)	17.9 (+0.2)	25.1 (−0.7)	6.6
52			25 [f]	2	96	10.5 (c)	22.5 (+0.4)	26.2 (−0.3)	3.7
53			−41	4	24	0.8 (c)	4.1 (−2.4)	9.7 (−0.8)	1.2
54		Ether	25	2	c	0.3 (c)	2.0 (−6.7)	4.6 (+0.3)	1.3
55			−41	4	c	0.3 (c)	0.8 (−8.2)	1.8 (−1.3)	0.4
56		Acetonitrile	25	2	54	21.1 (0.0)	1.9 (+0.4)	1.4 (+0.7)	0.4
57			−41	4	36	20.0 (−0.1)	2.5 (+0.1)	4.1 (−0.1)	1.1
58	**9a**	Pentane	27	2	71	0	7.6 (−0.2)	19.9 (−1.2)	6.1
59			−43	4	54	0	7.1 (+0.1)	18.1 (−0.1)	4.3
60		Toluene	27	2	95	0	21.4 (+0.4)	56.8 (−1.4)	20.4
61			−41	4	>99	0	19.6 (−0.4)	53.6 (−0.3)	13.0
62	**9b**	Toluene	25	2	>99	0	9.7 (+0.7)	26.2 (+1.0)	9.7
63			−41	4	95	0	11.3 (+0.4)	30.8 (+0.2)	7.5
64	**9c**	Toluene	25	2	>99	0	8.8 (+1.3)	22.3 (−1.3)	7.1
65			−41	4	>99	0	8.2 (+0.2)	21.2 (−0.3)	5.1
66	**10a**	Pentane	25	2	c	0	0.6 (+1.9)	1.4 (−1.0)	0.4
67			−39	3	21	0	0.3 (+1.2)	0.8 (−0.7)	0.2
68		Toluene	25	2	23	0	2.0 (+1.6)	5.0 (+1.1)	1.8
69			−41	3	52	0	1.3 (+0.1)	3.3 (−1.0)	0.9
70	**10b**	Toluene	25	2	23	0	2.5 (+0.8)	6.6 (−0.3)	2.5
71			−41	4	36	0	1.5 (+0.9)	3.8 (−0.5)	1.0
72	**10c**	Toluene	25	2	c	0	2.1 (−0.2)	5.4 (+0.6)	2.0
73			−41	4	39	0	1.9 (+0.3)	5.0 (−1.4)	1.2
74	**11a**	Pentane	25	2	12	0	0.4 (−2.3)	1.0 (−1.3)	0.3

Table 1 (Contd.)

Entry	Sensitizer	Solvent	Temperature/°C	Irradiation time/h	Conversion (%)	% yield (% ee[b])			
						2a	2b	3a	3b
75			−41	4	18	0	0.2([c])	0.5 (−1.2)	0.1
76		Toluene	28	2	16	0	2.8 (+0.9)	7.0 (+0.8)	2.6
77			−41	4	52	0	1.5 (−0.2)	3.5 (−0.3)	1.0
78	**11b**	Toluene	25	2	30	0	1.3 (−0.1)	3.2 (−0.2)	1.0
79			−41	4	62	0	1.0 (−1.4)	2.8 (+0.7)	0.7
80	**11c**	Toluene	25	2	26	0	2.4 (+0.2)	6.3 (0.0)	2.3
81			−41	4	61	0	2.3 (−1.5)	6.0 (+0.7)	1.7
82	**12a**	Toluene	25	2	53	0	1.7 (+0.4)	4.3 (−0.8)	1.6
83			−41	4	55	0	1.6 (+0.2)	4.2 (−1.0)	1.1

[a] $[1] = 100$ mmol dm^{-3}; [Sens*] = 5 mM unless noted otherwise. [b] Enantiomeric excess determined by chiral GC. [c] Not determined. [d] $[1] = 50$ mmol dm^{-3}. [e] $[1] = 20$ mmol dm^{-3}. [f] $[1] = 10$ mmol dm^{-3}.

respectively) gave **2b**, **3a** and **3b** in low chemical yields (**2b** and **3b** in <2%, **3a** in <5%), these yields were slightly enhanced in toluene, however no **2a** was formed in either pentane or toluene. The product ratios **2b**:**3a**:**3b** were 1.2:3.0:1.0 and 1.2:3.0:0.7 at 25 and −41 °C respectively, which are exactly the same as those obtained in the benzenepolycarboxylate sensitizations described above. This agreement suggests that the photocyclodimerizations of **1** sensitized by benzenecarboxylates **4a** and **5a**, and by naphthalenecarboxylates **6a** and **7a** proceed through a common intermediate such as a singlet biradical. Unfortunately, the photosensitizations with the naphthalenemonocarboxylates **6a–c** and **7a–c** gave practically racemic **2b** and **3a** in both pentane and toluene even at the low temperature.

Chemical yields were greatly improved upon sensitization with naphthalene-1,4- and 1,8-dicarboxylates **8a** and **9a** (runs 27–30 and 58–61), up to 14–20% for **2b** and **3b** and 41–57% for **3a**. But sensitization with naphthalene-2,3- and 2,6-dicarboxylates **10a** and **11a** (runs 66-69 and 74–77, respectively) was ineffective in enhancing the chemical yields, resulting in low ee's (< 2.5%) in all cases. In general, the use of toluene as solvent slightly enhanced the chemical yields but did not improve the products' ee. Judging from the facts that the product ratios obtained upon sensitization with **8a–11a** agree with those obtained with the benzenepolycarboxylates **4a** and **5a**, and that the *endo*-adduct **2a** was not formed under these conditions, we deduce that the photosensitization with the naphthalenedicarboxylates in non-polar solvents proceeds through the singlet energy-transfer mechanism involving a singlet biradical or other common intermediate, as is the case with the benzenepolycarboxylates. The ee's were not enhanced by using the (−)-8-phenylmenthyl naphthalenedicarboxylates **8b–11b** (runs 34–35, 62–63, 70–71 and 78–79, respectively). Neither chemical yield nor ee's were improved upon by using the highly substituted tetramenthyl naphthalenetetracarboxylate **12a** in toluene (runs 82–83). Based on these results we may conclude that the product ratio is independent of the energy and structure of sensitizers in non-polar solvents, and also that the simple singlet energy-transfer sensitization is ineffective in inducing chirality in the cyclodimers.

In order to elucidate the origin of the sensitizer-dependent chemical yields, we calculated the Rehm–Weller free energy change $(\Delta G_{et})^{28}$ from the oxidation potential of **1** (E_{ox} = 1.15 V),[20c] the reduction potentials (E_{red}) and fluorescence 0–0 bands (λ_{0-0}) of sensitizers **4a–12a**. The relevant data are listed in Table 2. The observed differences in photoreactivity are well accounted for in terms of the calculated ΔG_{et} values. Apart from the highly hindered naphthalene-1,2,3,4-tetracarboxylate **12a**,[29] the naphthalene-1,4- and 1,8-dicarboxylates **8a** and **9a** gave the most negative ΔG_{et} values among the sensitizers examined, which is the primary reason for the high chemical yields obtained upon sensitization with **8** and **9**. As the singlet energies of naphthalene(poly)carboxylates **6a–12a** are significantly

Table 2 Reduction potentials and calculated free energy change (ΔG_{et}) for electron transfer interaction of cyclohexa-1,3-diene **1** with chiral arene(poly)carboxylates **4–12a**

Sensitizer	$E_{red}{}^{a}$/V	$\lambda_{0-0}{}^{b}$/nm	$\Delta G_{et}{}^{c}$/kJ mol^{-1}
4a	[d]	315	—
5a	[d]	309	—
6a	−2.30	334	−5.2
7a	−2.39	339	8.8
8a	−1.84	371	−13.9
9a	−2.22	334	−12.9
10a	−2.30	341	2.2
11a	−2.02	357	−9.1
12a	−1.89	345	−33.7

[a] Reduction potentials estimated from the half-wave potentials measured using a platinum electrode, relative to the Ag/AgCl electrode using 0.1 mol dm^{-3} tetrabutylammonium perchlorate as the electrolyte in acetonitrile. [b] Fluorescence maxima of highest energy emission in frozen EPA (diethyl ether:isopentane:ethanol = 5:5:2) glass at 77 K. [c] Based on Weller equation: $\Delta G_{et} = 23.06\,(E_{ox}(D^{+}/D) - E_{red}(A/A^{-})) - \Delta G_{0-0} - w_p$; oxidation potential of **1** (E_{ox}) estimated as 0.028 V before the peak potential (E_p = 1.33 V [14a]); Coulombic attraction term (w_p) taken to be −5.4 kJ mol^{-1}. [d] Not determined due to low solubility of **4a** and **5a** in acetonitrile.

lower than those of benzenepolycarboxylates **4a** and **5a**, the simple singlet energy transfer mechanism cannot rationalize the photoreactivity, consequently we may conclude that the photocyclodimerization of **1** sensitized by naphthalene(poly)carboxylates (at least with **8** and **9**) proceeds through the electron transfer mechanism which involves an exciplex with high charge-transfer character or a contact ion pair even in the nonpolar solvents.

Effect of saccharide auxiliary

In our recent study,[15b] we demonstrated that the use of protected saccharides as chiral auxiliaries of the photosensitizer can enhance both the chemical and optical yields in the enantiodifferentiating photoaddition of alcohols to 1,1-diphenylalkene, through the increased 'microenvironmental polarity' around the sensitizer chromophore. In this context it is interesting to examine the effects of saccharide derivatives (**c–f**). The photocyclodimerizations of **1** sensitized by naphthalene(di)carboxylates **6c–11c**, which possess diacetone glucose (DAG) auxiliaries were first examined in pentane and in toluene (runs 17–18, 25–26, 36–38, 64–65, 72–73 and 80–81 respectively). Unexpectedly, the DAG ester chiral sensitizers **6c**, **7c**, **9c**, **10c** and **11c** did not particularly improve the chemical or optical yields, and the product ratios obtained were very similar to those for the menthyl esters **6a–11a**. However, the photosensitization with naphthalene-1,4-dicarboxylates with saccharide auxiliaries **8c–f** (runs 36–57) showed distinctly different behaviour in toluene. The *endo*-adduct **2a** which is derived from

the radical cation intermediate usually generated in polar solvent under the electron transfer conditions was obtained in low but appreciable yield, along with the slightly enhanced formation of **2b** (the average product ratio of **2b**:**3a**:**3b** is 1.3:3.0:1.1 and 1.3:3.0:0.7 at 25 and −41 °C, respectively). The ee of **2b** was increased to 7.6% upon sensitization with **8e** in toluene at 25 °C (run 45), whereas the **3a** obtained was practically racemic in any solvent and at any temperature examined. Unfortunately in most cases the ee of **2a** could not be determined by chiral GC as a result of low chemical yields, though **2a** obtained from toluene at −41 °C (run 42) was racemic.

In order to investigate the influence of solvent polarity, photosensitization by **8c**–**f** was performed in diethyl ether (runs 39–40, 43–44, 47–48, 54–55) and in acetonitrile (runs 56–57). In diethyl ether, the yield of **2a** relative to **3a** was slightly enhanced for all saccharide sensitizers and the highest ee (8.2%) was obtained for **2b** upon sensitization with **8f** in ether at −41 °C (run 55), although the ee of **3a** was not improved in polar solvents. In contrast, the photosensitization with menthyl ester **8a** in ether gave no *endo*-adduct **2a**, and the resulting product ratio is comparable to that obtained in non-polar solvent (runs 31 and 32). Hence, the formation of **2a** and the altered product ratios obtained upon sensitizations with saccharide esters are attributable to the enhanced microenvironmental polarity around the sensitizer chromophore. Under such conditions, the charge-transfer interaction is encouraged by the enhanced microenvironmental polarity, and the dissociation of the resulting radical ion pair is discouraged by the low bulk polarity. The combined effects keep the stereochemical interaction between chiral sensitizer and the substrate more intimate, resulting in increased ee's. Judging from the fact that the highest ee was obtained in ether, the enhancement of the microenvironmental polarity is not canceled by ether's lower bulk polarity. In acetonitrile the effect of the saccharide auxiliaries seems to disappear completely, as the photosensitization with both the methyl ester **8a** and the saccharide ester **8f** gave the electron-transfer product **2a** as the main product, and all of the chiral products obtained were racemic.

Effect of substrate concentration

The product ratio of the electron-transfer dimerization of **1** is known to be sensitive to the reaction conditions, *e.g.* solvent,[19,20c,f,30] concentration of **1**,[20c,f,24] wavelength[20c,22] and sensitizer.[20c] Upon sensitization with 1,4-dicyanonaphthalene or chloranil in acetonitrile the product ratio depends critically on the concentration of the substrate **1**, with the *endo*-isomer **2a** more favoured at lower concentrations. This has been accounted for in terms of the involvement of differently solvated radical ion pairs. At high concentration of **1**, the polarized exciplex or contact ion pair (CIP), which is formed after (partial) electron transfer from **1** to excited sensitizer, is efficiently quenched by a second molecule of **1** to afford *exo*-adduct **2b**. At low concentration of **1**, the CIP dissociates to solvent-separated ion pairs (SSIP), which in turn give *endo*-adduct **2a**.[20c,e] In the present study, we observed considerable concentration effects on the product distribution upon photosensitization with **8f** in diethyl ether (runs 49–52). Thus, on decreasing the concentration of **1** from 100 to 10 mmol dm⁻³, the *endo/exo* ratio (**2a**/**2b**) increased from 0.12 to 0.47. Since these results coincide exactly with the reported observations,[20c,e,24] it can be concluded that the electron-transfer mechanism operates in this reaction, and that the mechanism involves differently solvated radical-ion pairs. On the other hand, the ee of **2b** was reduced with decreasing concentration of **1**, and eventually no enantiodifferentiation was observed at concentrations less than 20 mmol dm⁻³ (runs 51 and 52), where the *endo*-isomer **2a** is favoured. It has been shown that a contact ion pair or exciplex with high charge-transfer character shows different selectivities in the photoinduced electron-transfer

Table 3 Fluorescence quenching of chiral sensitizers by cyclohexa-1,3-diene **1**[a]

Sensitizer	Solvent	$k_Q\tau/\text{mol}^{-1}\ \text{dm}^3$	τ^b/ns	$k_Q/10^{10}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$
6a	Pentane	21	0.78	2.7
7a	Pentane	87	8.0	1.1
8a	Pentane	88	3.6	2.4
	Acetonitrile	92	8.2	1.1
9a	Pentane	21	1.5	1.4
10a	Pentane	78	6.6	1.2
11a	Pentane	121	9.9	1.2
12a	Pentane	30	2.9	1.1

[a] Measured with 0.01 mmol dm⁻³ aerated solution of sensitizers at 25 °C. [b] Fluorescence lifetime of sensitizers in aerated solution at 25 °C.
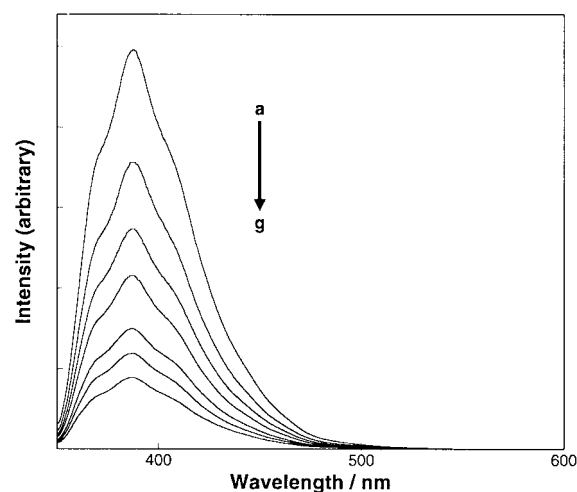
Fig. 1 Quenching of fluorescence of **8a** (1 mmol dm⁻³ in pentane), excited at 340 nm, by **1** at various concentrations: (a) 0, (b) 5, (c) 10, (d) 16, (e) 26, (f) 37, and (g) 52 mmol dm⁻³.

dimerization of **1**,[19,20b,c,d] compared to a solvent-separated ion pair or free radical cation. The *endo*-dimer **2a** is formed from the solvent-separated ion pair or free radical cation. Since the insufficiently cationic **1** in the contact ion pair or exciplex is not efficiently trapped by ground-state **1** at low concentrations, it thus tends to form a solvent-separated ion pair for which effective enantiodifferentiation is not expected to occur.

Quenching of sensitizer fluorescence

In order to elucidate the excited state and mechanism involved in the photosensitized cyclodimerization, fluorescence quenching experiments were performed with the menthyl esters **6a**–**12a** in aerated pentane and acetonitrile. The fluorescence of sensitizers was efficiently quenched upon the addition of **1** up to 100 mmol dm⁻³. Representative quenching behaviour of **8a** in pentane is shown in Fig. 1. Even at high concentrations of **1** no emission attributable to exciplex or triplex intermediates was observed for any sensitizer.

Using the conventional Stern–Volmer treatment of the quenching data [eqn. (1)], the relative fluorescence intensity

$$I_F^0/I_F = 1 + k_Q\tau^0\ [Q] \qquad (1)$$

(I_F^0/I_F) was plotted as a function of the concentration of **1** added, and an excellent straight line was obtained for each sensitizer, as exemplified in Fig. 2. From the Stern–Volmer constant ($k_Q\tau^0$) obtained from the slope of the plot and the fluorescence lifetime (τ^0) determined independently by using the single photon counting technique, the quenching rate constant (k_Q) for each sensitizer was calculated. The results are summarized in Table 3.
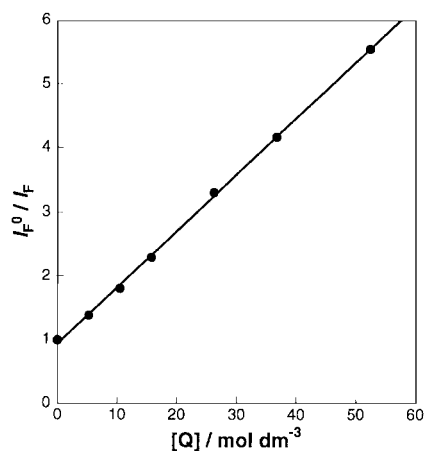
Fig. 2 Stern–Volmer plot for fluorescence quenching of **8a** by **1** in pentane.

The quenching of sensitizer singlet by **1** proceeds very efficiently at rates of $1.1–2.7 \times 10^{10}$ mol^{-1} dm^3 s^{-1}, which are almost comparable to the diffusion controlled rate in pentane ($k_{diff} = 4.4 \times 10^{10}$ mol^{-1} dm^3 s^{-1})[31] and acetonitrile ($k_{diff} = 2.9 \times 10^{10}$ mol^{-1} dm^3 s^{-1}).[31] Although no exciplex emission was observed, it is inferred that the quenching leads to an exciplex intermediate with high charge-transfer character, or directly to a contact radical ion pair in nonpolar solution. If the ΔG_{et} value is not sufficiently negative to develop a positive charge on **1**, the subsequent attack of the second **1** (forming a dimer biradical) should be decelerated, which should account for the low chemical yields obtained upon sensitization with **6a**, **7a**, **10a** and **11a**. Contrary to this, the much higher chemical yields obtained upon sensitization with **8a** and **9a** are attributable to the highly negative ΔG_{et} values for **8a** and **9a** and the accompanying development of positive charge on **1**, which accelerates the subsequent attack of **1**.

Mechanism

On the basis of the mechanism reported previously,[14b,19,20] we propose a modified mechanism illustrated in Scheme 2, which
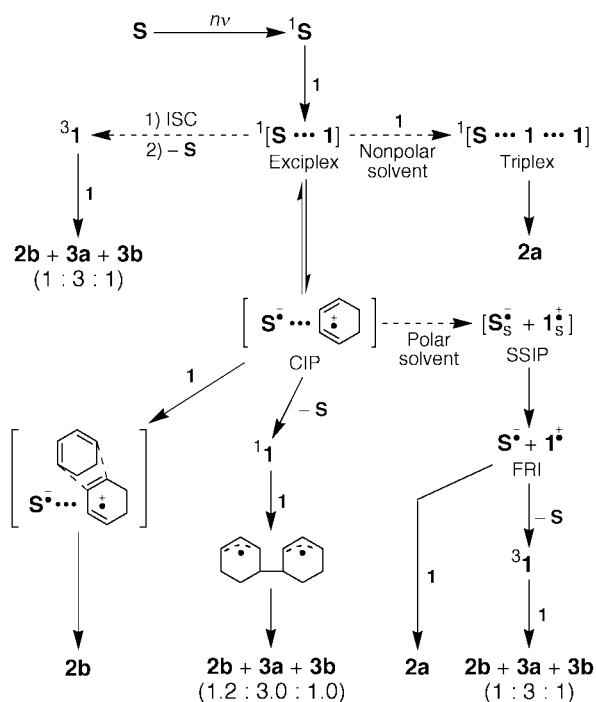
(ISC: intersystem crossing; CIP: contact ion pair; SSIP: solvent separated ion pair; FRI: free radical ions)

Scheme 2

is compatible with the previous and present results. In view of the relatively low concentrations of **1** (10–100 mmol dm^{-3}) employed in this study, we may exclude the serious contribution of the triplex intermediate,[14a–d,30] intervention of which has been proposed at much higher concentrations of 0.2–2 mol dm^{-3} in non-polar or less polar solvents.[14a–d]

Although the enantiodifferentiating photocyclodimerization of **1** sensitized by various chiral sensitizers can potentially give four isomeric cyclodimers **2a**, **2b**, **3a** and **3b** as described above, significant ee's were obtained exclusively for the *exo*-[4 + 2]-cyclodimer **2b** upon sensitization with saccharide esters **8c–f** in pentane or ether. This means that in addition to the biradical and radical ionic routes illustrated in Scheme 2, there is an independent cyclodimerization pathway that involves either the exciplex or contact ion pair of **1** with chiral sensitizer and affords preferentially **2b**. In the case of saccharide esters **8c–f**, the highly negative ΔG_{et} values and the enhanced microenvironmental polarity around the chromophore may stabilize such an exciplex or contact ion pair intermediate in nonpolar solvents, allowing the transfer of chiral information from the sensitizer to the cyclodimer. Because the product ratios obtained in nonpolar solvents do not greatly deviate from the average value (**2b**:**3a**:**3b** = 1.15: 3.00:1.02 and 1.17:3.00:0.74 at 25 and −41 °C, respectively) for most of the naphthalene(di)carboxylate sensitizers, except for the saccharide esters **8c–f**. Then, we may estimate the 'net' ee of **2b** produced through this 'independent' exciplex route by assuming that **2b**, **3a** and **3b** formed through the singlet biradical intermediate are racemic (or inherently achiral), and their ratio is fixed at 1.15:3.00:1.02, irrespective of the sensitizer and solvent used. Also that **2b** is produced exclusively through either the exciplex or singlet biradical mechanism, as demonstrated in the literature.[20,32] In the case of the photosensitization by **8e** in toluene at 25 °C, 19% of **2b** is estimated to be formed *via* the exciplex, with a 'net' ee of 40%. In the case of the photosensitization by **8f** in ether at 25 and −41 °C, 10 and 12% of **2b** is similarly estimated to be formed *via* the exciplex, and the 'net' ee's are 65% and 70%, respectively.

Finally, we would like to emphasize that although the overall ee's are not very high (<8%) in the present case as a result of the contamination from the racemic product of the other route, the introduction of polar saccharide moieties into the sensitizer can raise the ee of the product through the enhancement of the microenvironmental polarity around the sensitizer chromophore.

Experimental

General

Fluorescence lifetimes were measured with 1×10^{-5} mol dm^{-3} solution of sensitizers in aerated pentane or toluene by means of the time-correlated single-photon-counting method on a Horiba NAES-1100 instrument equipped with a pulsed H$_2$ light source. The radiation from the lamp was made monochromatic by a 10-cm monochromator, and the emission from sample solution was detected through a Toshiba UV-33, 35 or 37 filter.

Enantiomeric excesses of **2a**, **2b** and **3a** were determined by gas chromatography over a 30 m chiral capillary column (SUPELCO β-Dex325 and/or 120) at 100 °C, using a Shimadzu

GC-14B instrument connected to a Shimadzu C-R6A integrator. Calibrations with racemic **2a**, **2b** and **3a** indicated that the GC analysis gave a systematic error of ±0.8% ee.

Materials

Pentane used as solvent was stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aqueous sodium hydrogen carbonate, dried over sodium sulfate, and then fractionally distilled. Toluene was fractionally distilled from melting sodium. Diethyl ether was refluxed with potassium hydroxide and then fractionally distilled from sodium. Spectrograde acetonitrile (Dojin) was used without further purification. Cyclohexa-1,3-diene **1** (Aldrich) was purified by fractional distillation, followed by column chromatography on activated aluminum oxide (ICN Biomedicals).

Optically active alcohols used in the preparation of the sensitizers were commercially available: (−)-menthol from TCI; (−)-8-phenylmenthol from Aldrich.

Sugar derivatives were prepared from D-glucose and D-fructose according to the procedures reported by Kartha *et al.*[33] and Kang *et al.*,[34] respectively.[15b] 1,2:5,6-Di-*O*-cyclohexylidene-α-D-glucofuranose and 1,2:4,5-di-*O*-cyclohexylidene-β-D-fructopyranose were prepared in a similar manner. 1,2:5,6-Di-*O*-cyclohexylidene-α-D-glucofuranose: $[a]_D^{31}$ +3.51° (*c* 2.15, CHCl$_3$) (lit.[35] $[a]_D^{31}$ +1.65° (*c* 2.10, CHCl$_3$)); mp 139–140 °C; δ_H(CDCl$_3$) 1.24–1.87 (m, 20H), 2.60 (d, *J* = 2.9 Hz, 1H), 3.96 (dd, *J* = 2.9, 5.9 Hz, 1H), 4.06 (dd, *J* = 2.4, 4.9 Hz, 1H), 4.14–4.18 (m, 1H), 4.33–4.34 (m, 1H), 4.52 (d, *J* = 3.4 Hz, 1H), 5.95 (d, *J* = 3.4 Hz, 1H). 1,2:4,5-Di-*O*-cyclohexylidene-β-D-fructopyranose: $[a]_D^{25}$ −108.3° (*c* 0.52, CHCl$_3$); mp 130–131 °C; δ_H(CDCl$_3$) 1.59–1.79 (m, 20H), 3.64 (dd, *J* = 6.8, 8.3 Hz, 1H), 3.96 (d, *J* = 8.8 Hz, 1H), 4.01–4.05 (m, 2H), 4.10 (t, *J* = 2.4 Hz, 2H), 4.12–4.22 (m, 2H).

1-Cyanonaphthalene (TCI) and benzophenone (Wako) used as achiral sensitizers were purified by recrystallization from methanol. Optically active benzenepolycarboxylates employed as chiral sensitizers were prepared as reported previously.[36] Chiral naphthalene(di)carboxylates were prepared from the corresponding alcohols and acid chlorides, which were prepared from the corresponding carboxylic acids or anhydrides.[15b] While most of the carboxylic acids and anhydrides were commercially available: naphthalene-1-, -2- and -1,4-(di)carboxylic acid from Wako, naphthalene-1,8- and -2,3-dicarboxylic anhydride from TCI, naphthalene-2,6-dicarboxylic acid dipotassium salt from Aldrich, naphthalene-1,2,3,4-tetracarboxylic acid was obtained by the hydrolysis of the tetramethyl ester, which was prepared according to the procedures reported by Cadogan *et al.*[37]

(−)-1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl naphthalene-1-carboxylate (6c).

(Found: C, 66.41; H, 6.33. Calc. for C$_{23}$H$_{26}$O$_7$: C, 66.65; H, 6.32%); $[a]_D^{26}$ −36.1° (*c* 1.03, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2989, 1724, 1512, 1377, 1242, 1134, 1076, 849, 783, 509; λ_{max}(methylcyclohexane)/nm 211.6 (ε/dm^3 mol^{-1} cm^{-1} 37500), 218.4 (38700), 298.2 (7100); δ_H(CDCl$_3$) 1.31 (s, 3H), 1.35 (s, 3H), 1.45 (s, 3H), 1.58 (s, 3H), 4.12 (m, 2H), 4.38 (m, 2H), 4.74 (d, *J* = 3.9 Hz, 1H), 5.59 (d, *J* = 2.9 Hz, 1H), 5.97 (d, *J* = 3.9 Hz, 2H), 7.48–7.66 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.16 (dd, *J* = 1.5, 7.3 Hz, 1H), 8.93 (d, *J* = 8.3 Hz, 1H); *m/z* 414 (M$^+$, 7%), 399 (43), 272 (11), 255 (11), 172 (42), 155 (100), 127 (26), 101 (43).

(−)-1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl naphthalene-2-carboxylate (7c).

mp 106.0–107.0 °C (Found: C, 66.14; H, 6.05. Calc. for C$_{23}$H$_{26}$O$_7$: C, 66.65; H, 6.32%); $[a]_D^{26}$ −54.8° (*c* 1.02, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2989, 1724, 1631, 1462, 1377, 1269, 1200, 1095, 953, 872, 837, 764, 517; λ_{max}(methylcyclohexane)/nm 238.8 (ε/dm^3 mol^{-1} cm^{-1} 69700), 272.0 (7360), 280.6 (9110), 291.0 (6500), 320.0 (1480), 326.2 (1280), 334.8

(1980); δ_H(CDCl$_3$) 1.27 (s, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.58 (s, 3H), 4.14 (m, 2H), 4.41 (m, 2H), 4.69 (d, *J* = 3.4 Hz, 1H), 5.58 (d, *J* = 2.9 Hz, 1H), 6.01 (d, *J* = 3.4 Hz, 1H), 7.59 (m, 2H), 7.88–8.05 (m, 4H), 8.58 (s, 1H); *m/z* 414 (M$^+$, 1%), 399 (14), 326 (32), 172 (14), 155 (100), 127 (40), 101 (18).

(−)-Bis(1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranosyl) naphthalene-1,4-dicarboxylate (8d).

mp 152.0–153.0 °C (Found: C, 66.93; H, 6.97. Calc. for C$_{48}$H$_{60}$O$_{14}$: C, 66.96; H, 7.02%); $[a]_D^{27}$ −23.7° (*c* 1.01, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2938, 1725, 1514, 1453, 1368, 1248, 1166, 1119, 1027, 927, 848, 779; λ_{max}(methylcyclohexane)/nm 212.2 (ε/dm^3 mol^{-1} cm^{-1} 40100), 243.4 (27400), 318.0 (7800); δ_H(CDCl$_3$) 1.35–1.77 (m, 40H), 4.09 (m, 4H), 4.34 (m, 4H), 4.73 (d, *J* = 3.9 Hz, 2H), 5.67 (m, 2H), 5.97 (d, *J* = 3.4 Hz, 2H), 7.67 (dd, *J* = 3.4, 6.8 Hz, 2H), 8.06 (s, 2H), 8.83 (dd, *J* = 3.4, 6.3 Hz, 2H); *m/z* 860 (M$^+$, 74%), 831 (11), 817 (66), 762 (14), 538 (16), 521 (100), 495 (22), 423 (9), 239 (17), 199 (86), 181 (10), 154 (13), 141 (41).

(−)-Bis(1,2:4,5-di-*O*-cyclohexylidene-β-D-fructopyranosyl) naphthalene-1,4-dicarboxylate (8f).

mp 187.0–188.0 °C (Found: C, 67.70; H, 7.30. Calc. for C$_{48}$H$_{60}$O$_{14}$: C, 66.96; H, 7.02%); $[a]_D^{27}$ −180.5° (*c* 1.00, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2935, 1724, 1514, 1454, 1244, 1105, 933, 779; λ_{max}(methylcyclohexane)/nm 212.0 (ε/dm^3 mol^{-1} cm^{-1} 36400), 243.8 (25500), 320.2 (7430); δ_H(CDCl$_3$) 1.39–1.89 (m, 40H), 4.04 (m, 4H), 4.20 (m, 4H), 4.31 (m, 2H), 4.50 (dd, *J* = 4.9, 8.3 Hz, 2H), 5.50 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 3.4, 6.8 Hz, 2H), 8.18 (s, 2H), 8.87 (dd, *J* = 3.4, 6.8 Hz, 2H); *m/z* 860 (M$^+$, 27%), 817 (6), 538 (18), 521 (96), 424 (9), 239 (8), 216 (10), 199 (100), 154 (12), 110 (9).

(+)-Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) naphthalene-1,8-dicarboxylate (9c).

mp 169.0–170.0 °C (Found: C, 61.49; H, 6.15. Calc. for C$_{36}$H$_{44}$O$_{14}$: C, 61.71; H, 6.33%); $[a]_D^{26}$ +55.3° (*c* 1.01, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2989, 1724, 1381, 1269, 1207, 1157, 1076, 1018, 845, 779, 640, 513; λ_{max}(methylcyclohexane)/nm 225.2 (ε/dm^3 mol^{-1} cm^{-1} 35900), 294.0 (7940); δ_H(CDCl$_3$) 1.41 (s, 6H), 1.42 (s, 6H), 1.44 (s, 6H), 1.55 (s, 6H), 4.09 (m, 2H), 4.23–4.37 (m, 4H), 4.54 (m, 2H), 5.07 (d, *J* = 3.4 Hz, 2H), 5.45 (d, *J* = 2.9 Hz, 2H), 6.03 (d, *J* = 3.9 Hz, 2H), 7.56 (m, 2H), 8.02 (m, 4H); *m/z* 700 (M$^+$, <1%), 685 (100), 443 (15), 441 (16), 401 (17), 243 (20), 213 (12), 199 (47), 185 (64), 155 (28), 127 (56), 113 (49), 101 (97).

(−)-Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) naphthalene-2,3-dicarboxylate (10c).

mp 178.5–179.5 °C (Found: C, 61.80; H, 5.87. Calc. for C$_{36}$H$_{44}$O$_{14}$: C, 61.71; H, 6.33%); $[a]_D^{26}$ −61.9° (*c* 1.04, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2989, 1736, 1462, 1377, 1257, 1211, 1072, 852, 783, 513; λ_{max}(methylcyclohexane)/nm 239.4 (ε/dm^3 mol^{-1} cm^{-1} 54200), 271.8 (5320), 281.4 (5120), 323.2 (1160), 336.2 (1480); δ_H(CDCl$_3$) 1.34 (s, 6H), 1.38 (s, 6H), 1.44 (s, 6H), 1.57 (s, 6H), 4.08 (m, 4H), 4.35 (m, 4H), 4.85 (d, *J* = 3.4 Hz, 2H), 5.50 (m, 2H), 5.99 (d, *J* = 3.9 Hz, 2H), 7.67 (dd, *J* = 2.9, 6.4 Hz, 2H), 7.93 (dd, *J* = 3.4, 5.9 Hz, 2H), 8.24 (s, 2H); *m/z* 700 (M$^+$, <1%), 685 (81), 569 (11), 459 (11), 441 (26), 401 (25), 283 (28), 325 (15), 213 (15), 199 (43), 185 (41), 155 (30), 127 (53), 113 (71), 101 (100).

(−)-Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl) naphthalene-2,6-dicarboxylate (11c).

mp 106.5–107.5 °C (Found: C, 61.88; H, 6.76. Calc. for C$_{36}$H$_{44}$O$_{14}$: C, 61.71; H, 6.33%); $[a]_D^{26}$ −71.7° (*c* 1.03, CHCl$_3$); ν_{max}(KBr)/cm^{-1} 2989, 1720, 1377, 1261, 1219, 1173, 1084, 1022, 845, 768, 636, 513; λ_{max}(methylcyclohexane)/nm 224.8 (ε/dm^3 mol^{-1} cm^{-1} 24900), 244.4 (82800), 274.4 (8950), 284.0 (14000), 294.6 (13800), 335.0 (2330), 351.0 (2970); δ_H(CDCl$_3$) 1.27 (s, 6H), 1.34 (s, 6H), 1.43 (s, 6H), 1.58 (s, 6H), 4.14 (m, 4H), 4.38 (m, 4H), 4.69 (d, *J* = 3.9 Hz, 2H), 5.90 (d, *J* = 2.9 Hz, 2H), 6.01 (d, *J* = 3.9 Hz, 2H), 8.03 (d, *J* = 8.3 Hz, 2H), 8.12 (d, *J* = 8.3 Hz, 2H), 8.61 (s, 2H); *m/z* 700 (M$^+$, <1%), 685 (75), 541 (14), 441 (88), 199 (40), 154 (18), 101 (100).

(−)-Tetramenthyl naphthalene-1,2,3,4-tetracarboxylate (12a).
mp 160.0–161.0 °C (Found: C, 75.60; H, 9.41. Calc. for
$C_{54}H_{80}O_8$: C, 75.66; H, 9.41%); $[a]_D^{26}$ −162.9° (c 1.02, $CHCl_3$);
ν_{max}(KBr)/cm^{-1} 2954, 1732, 1454, 1373, 1215, 957; λ_{max}(methyl-
cyclohexane)/nm 239.6 (ε/dm^3 mol^{-1} cm^{-1} 53200), 288.6 (6670),
334.4 (1130); δ_H($CDCl_3$) 0.78–0.90 (m, 28H), 0.97 (d, $J = 6.4$
Hz, 6H), 1.01 (d, $J = 6.4$ Hz, 6H), 1.14 (s, 8H), 1.41–1.75
(m, 16H), 2.02 (m, 4H), 2.35 (m, 2H), 2.53 (m, 2H), 4.80 (dt,
$J = 4.4$, 10.7 Hz, 2H), 5.00 (dt, $J = 4.4$, 10.5 Hz, 2H), 7.64 (dd,
$J = 3.2$, 6.6 Hz, 2H), 7.98 (dd, $J = 3.2$, 6.6 Hz, 2H); m/z 879
(M^+ + Na, 6%), 855 (2), 305 (50), 287 (78), 269 (21), 137 (42),
123 (13).

Photolysis

All irradiations were performed in a temperature-controlled
water (25 °C), methanol–propan-2-ol (−40 °C) bath. The light
sources employed were a conventional 300 W high-pressure
mercury lamp for irradiations at 25 °C and an equivalent lamp
fitted with a transparent Pyrex vacuum sleeve designed for low-
temperature irradiation (Eikosha). A solution (4 cm^3), contain-
ing cyclohexa-1,3-diene **1** (100 mmol dm^{-3}), optically active
sensitizer **4**–**12** (5 mmol dm^{-3}), and *n*-dodecane (5 mmol dm^{-3})
added as an internal standard, was irradiated at >300 nm under
an argon atmosphere in a Pyrex tube (1 cm i.d.) placed near the
lamp surface or in an annular Pyrex vessel surrounding the
lamp, the whole system being immersed in the cooling bath.

Acknowledgements

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Paper a906826k