Enantiodifferentiating photoisomerization of (*Z*)-cyclooctene and (*Z*,*Z*)-cycloocta-1,3-diene sensitized by chiral aromatic amides

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Optically active benzene(poly)carboxamides with C_2-symmetric pyrrolidine moieties have been employed as chiral sensitizers for the geometrical photoisomerizations of (*Z*)-cyclooctene (1*Z*) and (*Z*,*Z*)-cycloocta-1,3-diene (1*ZZ*) in some solvents at varying temperatures. *ortho*-Substituted di- and tetra-amides used as chiral sensitizers give enantiomeric excesses (ee) up to 14% for both 1*Z* and 1*ZZ* in pentane at low temperatures. The use of polar solvents dramatically diminishes the product's ee, due to the intervention of a free or solvent-separated radical ion pair between 1 and the chiral sensitizer.

Introduction

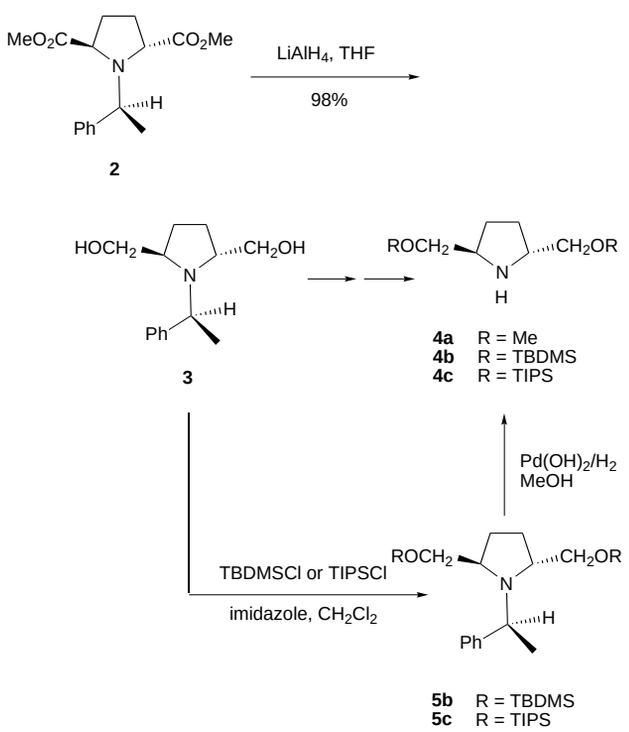
Asymmetric photosensitization, which enables *catalytic* asymmetric synthesis in the excited state, has attracted much attention for more than three decades.[1,2] However, in spite of the considerable efforts devoted to photochemical studies employing various chiral sensitizers and prochiral substrates,[1,2] only a limited number of enantiodifferentiating photosensitizing systems[3–5] have been known to give the product's enantiomeric excess (ee) better than the original ee (6.7%) reported by Hammond and Cole in 1965.[6] Of the successful systems, the photosensitized enantiodifferentiating isomerizations of (*Z*)-cyclooctene (**1*Z***)[3a–c] and (*Z*,*Z*)-cycloocta-1,3-diene (**1*ZZ***)[3d] are of particular interest to us, since the sensitization with chiral aromatic esters gives exceptionally high ee's (up to 64%) and shows unique temperature effects that lead to unprecedented temperature switching behavior of the product chirality.

Since a wide variety of optically active alcohols are available from the chiral pool, we have hitherto employed aromatic carboxylic esters as chiral sensitizers, in which various naturally occurring and synthesized optically active alcohols were incorporated in the ester moiety as chiral auxiliaries.[3,5] In the course of exploring novel chiral sensitizers, we found that optically active benzene(poly)carboxamides, another important derivative of carboxylic acid, also function as chiral sensitizers for the enantiodifferentiating isomerization of both **1*Z*** and **1*ZZ***. In the present study, C_2-symmetric pyrrolidine derivatives were selected as the chiral amino auxiliaries, since the C_2-symmetric pyrrolidine ring bearing two identical groups at the 2- and 5-positions has been demonstrated to be notably effective as chiral auxiliary at least in thermal enantioselective syntheses, affording ee's near 100% in several important reactions.[7] In this approach, we first synthesized some (novel) *trans*-2,5-disubstituted pyrrolidine derivatives, from which a series of optically active benzene(poly)carboxamides were prepared. Then, the sensitizing and enantiodifferentiating abilities of these chiral aromatic amides were examined in the photosensitized geometrical isomerizations of **1*Z*** and **1*ZZ***.

Results and discussion

Synthesis

Optically pure pyrrolidine derivatives **2** and **3** and C_2-symmetric pyrrolidine **4a** were prepared according to the reported procedures.[8] The optically pure C_2-symmetric pyrrolidines **4b** and **4c** were synthesized in 95% yield in the reactions of **3** with *tert*-butyldimethylsilyl (TBDMS) chloride and triisopropylsilyl (TIPS) chloride, respectively, in the presence of imidazole, followed by catalytic hydrogenolysis of the immediate precursors **5b** and **5c** over palladium hydroxide in 80% yield, as illustrated in Scheme 1.

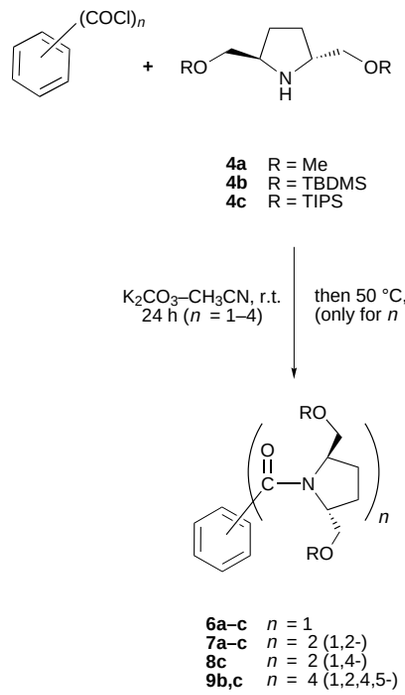


Scheme 1

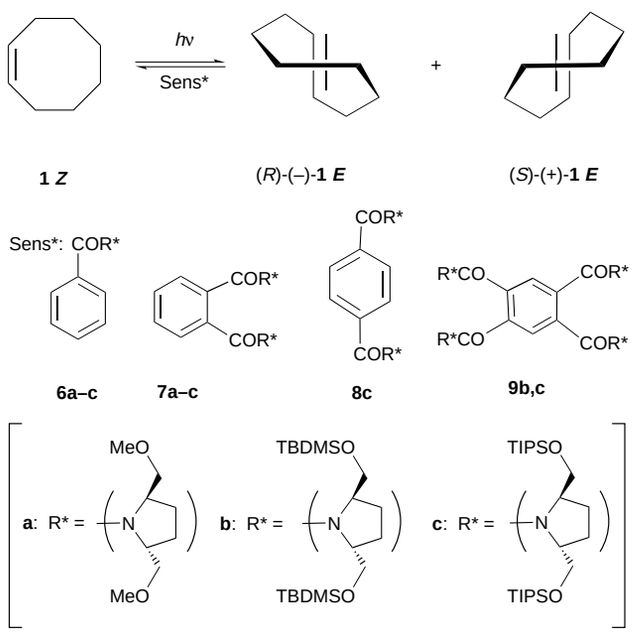
The optically active benzene(poly)carboxamides **6a**–**c**, **7a**–**c**, **8c** and **9b**,**c** with C_2-symmetric pyrrolidine moieties were readily synthesized in moderate to good yields in the reactions of the corresponding aroyl chlorides with **4a**–**c** in acetonitrile in the presence of potassium carbonate (Scheme 2).

Photoisomerization

Enantiodifferentiating photosensitizations of **1*Z*** and **1*ZZ*** were performed under various irradiation conditions in the presence of chiral aromatic amides prepared as above (Schemes 3 and 4). The major photochemical reaction observed was the *Z*–*E* isomerization of cyclooctene and cyclooctadiene, as was the case with the corresponding aromatic esters. Thus, the aromatic amides, possessing isoelectronic structures with the esters, were shown to function as effective sensitizers for the geometrical photoisomerization of simple alkenes, although the *E*/*Z* ratios obtained were smaller in general than those obtained with the



Scheme 2



Scheme 3

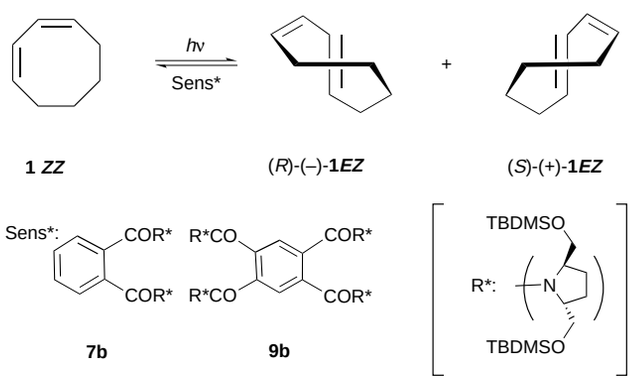
aromatic esters. The (*E*)-isomer produced was isolated from the photolyzate through the selective extraction of **1*E*** or **1*EZ*** with aqueous silver nitrate in >96% chemical yield.[9] Gas chromatographic analyses indicated that the isolated **1*E*** or **1*EZ*** contained a small amount (<2%) of **1*Z*** or **1*ZZ***. Enantiomeric excesses of **1*E*** and **1*EZ*** isolated were determined by gas chromatographic analysis on a chiral capillary column.

Enantiodifferentiation

The effects of irradiation period, or conversion, upon the product's yield and ee were first examined. As can be seen from Table 1, the *E*/*Z* ratio increases with increasing irradiation time, ultimately giving the photostationary-state *E*/*Z* ratio upon prolonged irradiations. In contrast, the product's ee is not appreciably affected by the irradiation time at least at the initial stages. Thus, the sensitization with **7b** gives practically constant ee's of 1.8 ± 0.5 and 7.0 ± 0.5% at 25 and −56 °C, respectively; these standard deviations obtained are well within the experimental error in the determination by chiral GC (±1% ee). However, appreciable deviations to slightly higher ee's are observed upon prolonged irradiation at −56 °C.

Table 1 Enantiodifferentiating photoisomerization of (*Z*)-cyclooctene (**1*Z***) sensitized by chiral aromatic amide (**7b**) in pentane

T/°C	*t*/h	*E*/*Z*	Conversion (%)	Yield (%)	Ee (%)
25	2	0.018	5.3	1.7	+1.0
	3	0.052	10.7	4.7	+2.2
	4	0.062	11.4	5.5	+2.0
	5	0.085	17.3	7.0	+2.3
	6	0.095	13.3	8.2	+1.5
	7	0.106	14.7	9.1	+1.5
−56	5	0.013	4.0	1.2	+6.2
	9	0.030	9.0	2.8	+7.2
	13	0.035	8.0	3.2	+6.9
	17	0.039	9.4	3.6	+7.1
	20	0.031	8.0	3.0	+7.6
	24	0.050	11.0	4.5	+9.0
	27	0.047	11.3	4.2	+8.4
	30	0.049	12.0	4.3	+9.0



Scheme 4

Hence, the irradiations were continued for a relatively long time in most cases to afford apparent photostationary-state mixtures, which were subjected to the selective extraction and the subsequent determination of ee by chiral GC. The results of enantiodifferentiating photosensitizations of **1*Z*** and **1*ZZ*** are summarized in Tables 2 and 3, respectively.

The number and position of introduced amide group(s) and the structure of the chiral auxiliary significantly affect the *E*/*Z* ratio and product's ee. In the photosensitization of **1*Z***, the *E*/*Z* ratio, as well as the conversion and the chemical yield, decrease with increasing number of amide substitution, for which lower singlet energies of the benzenepolyamides, resulting from the extended conjugation, should be responsible. In contrast, the use of diene **1*ZZ*** as a substrate, which possesses much lower singlet energy than **1*Z***, affords greatly improved *E*/*Z* ratios and yields upon sensitization with pyromellitamide **9b** (Table 3).

In the enantiodifferentiating photoisomerization of **1*Z*** in pentane, benzamides **6a**–**c** and terephthalamide **8c** used as chiral sensitizers merely afforded **1*E*** of extremely low ee's (0–3%) even at the low temperatures. In contrast, the *ortho*-substituted di- or tetra-amides **7** and **9** gave optically active **1*E*** in only 1–3% ee at 25 °C but much enhanced ee's of 7–14% at −56 °C under comparable irradiation conditions.

Analogous temperature dependence has been reported in the enantiodifferentiating photoisomerization of **1*Z*** sensitized by the corresponding aromatic esters,[3] although no temperature switching of the product chirality was observed in the present sensitizations with aromatic amides. We have suggested that, on the basis of molecular orbital calculations, the excited-state interaction of the π bond of **1*Z*** with the ester's C=O rather than aromatic C=C bond plays an important role in the enantiodifferentiating photoisomerization of **1*Z*** sensitized by chiral

Table 2 Enantiodifferentiating photoisomerization of (*Z*)-cyclooctene (**1*Z***) sensitized by chiral aromatic amides (**6**–**9**) in some solvents

Sensitizer	Solvent	*T*/°C	*t*/h	*E*/*Z*	Conversion (%)	Yield (%)	Ee (%)
6a	Pentane	25	2	0.10	25.0	7.5	+0.3
		−56	4	0.06	20.0	5.0	+0.3
6b	Pentane	25	2	0.17	27.6	12.5	−0.3
		−56	6	0.08	24.0	6.0	+0.1
6c	Pentane	25	2	0.16	22.0	13.0	−0.8
		−56	8	0.15	18.7	12.1	−0.5
7a	Pentane	25	3	0.11	22.5	8.2	+0.5
		−56	20	0.06	7.5	5.3	+7.6
7b	Pentane	25	5	0.09	17.3	7.0	+2.3
		−56	17	0.04	9.4	3.6	+7.1
7c	Pentane	25	4	0.07	11.3	6.0	+2.0
		−56	10	0.06	8.5	5.3	+7.8
8c	Pentane	25	6	0.08	23.0	6.3	+0.7
		−56	12	0.02	7.7	1.4	+2.7
9b	Pentane	25	5	0.02	5.3	2.1	+3.3
		−56	24	0.01	0.8	0.7	+14.0
	THF	25	3	0.01	1.2	1.0	−0.3
		−55	9	0.05	9.0	4.3	−0.3
	Diethyl ether	−52	12	0.01	9.7	0.5	+0.6
	Ethanol	25	6	0.01	2.0	1.0	−0.6
		−52	18	0.03	3.5	2.5	+0.1
9c	Pentane	25	4	0.02	4.3	1.9	+2.6
		−56	23	0.01	4.2	1.3	+12.0

Table 3 Enantiodifferentiating photoisomerization of (*Z*,*Z*)-cycloocta-1,3-diene (**1*ZZ***) sensitized by **7b** and **9b** in pentane

Sensitizer	*T*/°C	*t*/h	*E*/*Z*	Conversion (%)	Yield (%)	Ee (%)
7b	25	3	0.018	4.7	1.7	+0.8
	−67	3	0.063	8.2	5.8	+1.2
9b	25	2	0.031	8.6	3.0	+2.4
	−67	2	0.122	18.7	10.0	+14.3

aromatic esters, and also that the dynamic conformational changes of the adjacent bulky ester moieties of the *ortho*-substituted benzenepolycarboxylates, synchronized with the enantiodifferentiating rotational relaxation of **1*Z***'s double bond within the exciplex intermediate, is responsible for such a drastic temperature effect upon ee.[3b,c] The synchronized dynamic conformational changes characteristic of the *ortho* esters have been related to the anomalously high differential entropy of activation, determining the product's ee and its temperature dependence.[3b,c] In this context, the present tertiary amides possessing 2,5-disubstituted pyrrolidine are apparently more sterically hindered than any other benzenepolycarboxylates, which interferes with the dynamic conformation changes of the adjacent dialkylamino groups of *ortho*-substituted aromatic amides **7a**–**c** and **9b**,**c** and eventually reduces the temperature dependence as well as the product's ee. The higher electron donating ability of the nitrogen atom in the amide may enhance conjugation with the carbonyl group, diminishing the conformational flexibility of the peripheral alkyl groups. Unfortunately, these amides **6**–**9** are not fluorescent at all, and therefore no direct insights into the excited states of these aromatic amides and their interaction with **1*Z*** in the excited state are available.

In contrast to the severe effects of the steric hindrance around the amide C=O, the peripheral modification of the pyrrolidine ring does not appear to affect the product's ee. Thus, the phthalamides **7a**–**c**, possessing distinctly different peripheral groups from methyl to bulky *tert*-butyldimethylsilyl and triisopropylsilyl, gave comparable ee's at both 25 and −56 °C. Quite similar ee's were obtained also with pyromellitamides **9b** and **9c**.

Interestingly, the enantiodifferentiating photoisomerization of cycloocta-1,3-diene **1*ZZ*** sensitized by **9b** gave improved chemical yields and ee's comparable to those obtained for cyclooctene **1*Z***,[3d] although the sensitization with **7b** afforded much lower ee of 1.2% even at −67 °C, as shown in Table 3. The high ee (14.3%) and chemical yield (53% based on consumed **1*ZZ***) of **1*EZ*** were achieved by using bulky **9b** as chiral sensitizer at a low temperature. This ee is comparable to the highest value (17.6%) obtained in the photosensitization of **1*ZZ*** with (−)-hexamenthyl benzenehexacarboxylate in pentane at −40 °C.[3d]

Dramatic solvent effects upon chemical and optical yields were observed in the photosensitization of **1*Z*** with **9b**. As can be seen from Table 2, the effects of solvent polarity are ambivalent. The use of polar solvents such as diethyl ether, THF and ethanol leads to much lower chemical yields at 25 °C but higher yields at lower temperatures,while the product's ee dramatically decreases to almost nothing in polar solvents irrespective of the irradiation temperature. The lower ee's in polar solvents may reasonably be accounted for in terms of the intervention of a free or solvent-separated radical ion pair ($\mathbf{1Z}^{\bullet+} \cdots \mathbf{S}^{\bullet-}$) generated through the electron transfer from **1*Z*** to excited sensitizer (**S***) and the subsequent ion separation, both of which are facilitated in polar solvents. In such a separated radical ion pair, the chiral sensitizer $\mathbf{S}^{\bullet-}$ is located away from the substrate $\mathbf{1Z}^{\bullet+}$ and therefore not expected to contribute to the chiral recognition. Such drastic solvent effects have not been observed in the photosensitization of **1*Z*** with aromatic esters.[3] For instance, the sensitization of **1*Z*** by a corresponding aromatic ester with different chiral moiety, *i.e.* (−)-tetramenthyl benzene-1,2,4,5-tetracarboxylate, has been reported to give **1*E*** of −9.4, −7.4, −8.4 and −7.1% ee at 25 °C in pentane, diethyl ether, acetonitrile and ethanol, respectively.[3b] Hence, the exciplex intermediate resulting from **1*Z*** and aromatic amide sensitizer is inferred to possess higher charge-transfer character to facilitate ionization in polar solvents. Thus, it is confirmed that the photochemical reactions involving electron transfer are not specifically advantageous from the viewpoint of optical yield, but even such a sensitizer-substrate pair can give good optical yields if the solvent polarity is strictly controlled to prevent generation of a free or solvent-separated radical ion pair.

Experimental

General

Melting points were measured with a Yanaco MP-500D micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were determined for solutions in $CDCl_3$ containing tetra-

methylsilane as an internal standard on a JEOL JNM-EX400 spectrometer. *J* values are given in Hz. Mass spectra were recorded with a JEOL JMS D-300 instrument. Optical rotations were determined at 589 nm in a thermostatted conventional 10 cm cell, using a Perkin-Elmer Model 341 polarimeter. Combustion analyses of all new compounds were performed on a Perkin-Elmer Model 240 analyzer.

Gas chromatographic analyses of the geometrical isomers **1*Z***, **1*E***, **1*ZZ*** and **1*EZ*** in photolyzed solutions were performed on a 50 m capillary column (Shimadzu CBP20) at 65 °C on a Shimadzu 14A instrument. Enantiomeric excesses of **1*E*** and **1*EZ*** isolated through the selective extraction with 20% aqueous silver nitrate were determined by gas chromatography over a 60 m chiral capillary column (Supelco β-DEX 120) at 70 °C, using a Shimadzu 14A instrument.

Photolysis of 1*Z*

All irradiations were carried out in a temperature-controlled water (25 °C) or propan-2-ol (−25 to −78 °C) bath. A pentane solution (3 ml) containing **1*Z*** (5 mM), optically active sensitizer (1 mM) and cyclooctane (5 mM) added as an internal standard was irradiated at 254 nm under argon atmosphere in a quartz tube, using a 120 W low-pressure mercury lamp (Eikosha) fitted with a Vycor sleeve.

Photolysis of 1*ZZ*

All irradiations were carried out under similar conditions to those described above, except for the vessel and the light source. Since the product **1*EZ*** weakly absorbs the 254 nm resonance line of a low pressure mercury lamp, we employed a Pyrex tube (>280 nm) and a 300 W high-pressure mercury lamp (Eikosha).

Materials

1-[(*S*)-1-Phenethyl]-(2*R*,5*R*)-bis(*tert*-butyldimethylsiloxymethyl)pyrrolidine (5b). Compound **5b** was prepared by the reaction of **3** (2.0 g, 8.5 mmol) with *tert*-butyldimethylsilyl chloride (2.78 g, 18.5 mmol) in the presence of imidazole (1.36 g, 20 mmol) in dichloromethane. After usual workup, the residue was subjected to flash chromatography (SiO_2, eluted with ethyl acetate–hexane, 1:4) to give **5b** as colorless oil. Yield: 3.71 g (95%); $[\alpha]_D^{20}$ +25.1 (*c* 1, CH_2Cl_2); $\delta_H(CDCl_3)$ 0.07 (6H, s, Si-CH_3), 0.09 (6H, s, Si-CH_3), 0.83 [18H, s, Si-C$(CH_3)_3$], 1.45 (3H, d, *J* 6.8, CH_3), 1.60–1.70 (2H, m), 1.80–2.0 (2H, m), 3.10–3.20 (4H, m, CH_2), 3.23 (2H, dd, *J* 5.9, 3.2), 4.03 (1H, q, *J* 6.8), 7.20–7.50 (5H, m, Ar) (Found: M^+, 463.3301. Calc. for $C_{26}H_{49}Si_2NO_2$: 463.3304; Found: C, 67.24; H, 10.52; N, 2.97. Calc. for $C_{26}H_{49}Si_2NO_2$: C, 67.33; H, 10.65; N, 3.02%).

1-[(*S*)-1-Phenethyl]-(2*R*,5*R*)-bis(triisopropylsiloxymethyl)-pyrrolidine (5c). Compound **5c** was prepared in the same manner as described above. Yield: 4.82 g (96%); $[\alpha]_D^{20}$ +31.1 (*c* 1, CH_2Cl_2); $\delta_H(CDCl_3)$ 0.98 (24H, d, CH_3), 1.05 (12H, d, CH_3), 1.06 (6H, sept, CH), 1.48 (3H, d, *J* 6.8, CH_3), 1.80–2.0 (4H, m, CH_2), 3.15–3.20 (2H, m, CH_2), 3.23 (2H, t, *J* 8.8), 3.45 (2H, dd, *J* 9.3, 3.9), 4.0 (1H, q, *J* 6.8), 7.18–7.40 (5H, m, Ar) (Found: M^+, 547.4236. Calc. for $C_{32}H_{61}Si_2NO_2$: 547.4243; Found: C, 70.24; H, 11.12; N, 2.57. Calc. for $C_{32}H_{61}Si_2NO_2$: C, 70.14; H, 11.22; N, 2.56%).

(2*R*,5*R*)-Bis(*tert*-butyldimethylsiloxymethyl)pyrrolidine (4b). Compound **4b** was prepared by catalytic hydrogenolysis of **5b** over palladium hydroxide in methanol. Yield: 80%; $[\alpha]_D^{20}$ +10.4 (*c* 1.17, CH_2Cl_2); $\delta_H(CDCl_3)$ 0.10 (12H, s, Si-CH_3), 0.90 [18H, s, Si-C$(CH_3)_3$], 1.30–1.50 (2H, m), 1.80–1.95 (2H, m), 1.96 (1H, s), 3.25 (2H, quintet), 3.45 (4H, dd, *J* 5.86, 3.20) (Found: M^+, 359.2668. Calc. for $C_{18}H_{41}Si_2NO_2$: M, 359.2677; Found: C, 60.15; H, 11.45; N, 3.86. Calc. for $C_{18}H_{41}Si_2NO_2$: C, 60.11; H, 11.49; N, 3.90%).

(2*R*,5*R*)-Bis(triisopropylsiloxymethyl)pyrrolidine (4c). Compound **4c** was prepared by catalytic hydrogenolysis of **5c** over palladium hydroxide in ethanol. Yield: 80%; $[\alpha]_D^{20}$ +9.4 (*c* 1.0, CH_2Cl_2); $\delta_H(CDCl_3)$ 1.02 (36H, d, *J* 3.4, CH_3), 1.12 (6H, sept, CH), 1.40–1.54 (2H, m), 1.80–1.95 (2H, m), 3.30–3.40 (2H, m, CH_2), 3.61 (4H, dd, *J* 5.9, 3.2, CH_2) (Found: M^+, 443.3610. Calc. for $C_{24}H_{53}Si_2NO_2$: M, 443.3617; Found: C, 64.82; H, 12.01; N, 3.06. Calc. for $C_{24}H_{53}Si_2NO_2$: C, 64.95; H, 12.04; N, 3.16%).

Synthesis of chiral sensitizers 6a–c, 7a–c, 8c and 9b,c. *Benzamide* **6a**.—Compound **6a** was prepared by the reaction of **4a** (420 mg, 2.64 mmol) with benzoyl chloride (406 mg, 2.90 mmol) in acetonitrile in the presence of potassium carbonate (400 mg, 2.9 mmol) at room temperature. After usual workup, the residue was purified by flash chromatography (SiO_2, eluted with ethyl acetate–hexane, 1:4) to give **6a** as a light yellow oil. Yield: 560 mg (82%); $[\alpha]_D^{20}$ +140.1 (*c* 1, CH_2Cl_2); λ_{max}(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 3540); ν_{max}(neat)/cm^{-1} 1630 (C=O); $\delta_H(CDCl_3)$ 1.80–2.07 (3H, m), 2.08–2.30 (1H, m), 2.89 (1H, dd, *J* 9.0, 3.5), 2.98 (1H, t, *J* 9.0), 3.0 (3H, s, OCH_3), 3.40 (3H, s, OCH_3), 3.54 (1H, t, *J* 9.0), 3.60 (1H, dd, *J* 9.0, 3.5), 4.10–4.22 (1H, m), 4.42–4.50 (1H, m), 7.30–7.42 (3H, m, Ar), 7.42–7.60 (2H, m, Ar); *m*/*z* (FAB) 264 (M^+ + 1) (Found: C, 68.66; H, 8.16; N, 5.16. Calc. for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32%).

Phthalamide **7a**.—Compound **7a** was prepared by the reaction of **4a** (800 mg, 5.03 mmol) with phthaloyl chloride (487 mg, 2.4 mmol) in the same manner as described above. Yield: 400 mg (20%); mp 96–98 °C; $[\alpha]_D^{20}$ +215.6 (*c* 1, CH_2Cl_2); λ_{max}-(CH_3CN)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 5790); ν_{max}(KBr)/cm^{-1} 1630 (C=O); $\delta_H(CDCl_3)$ 1.95–2.23 (8H, m, CH_2), 3.0 (6H, s, OCH_3), 3.13 (2H, t, *J* 9.8), 3.28 (2H, dd, *J* 10.2, 3.0), 3.40 (6H, s, OCH_3), 3.51 (2H, dd, *J* 9.0, 6.8), 3.62 (2H, dd, *J* 9.0, 3.4), 4.06–4.16 (2H, m), 4.38–4.20 (2H, m), 7.38–7.43 (4H, m, Ar); *m*/*z* (FAB) 449 (M^+ + 1) (Found: C, 64.14; H, 8.05; N, 6.30. Calc. for $C_{24}H_{36}N_2O_6$: C, 64.26; H, 8.09; N, 6.25%).

Benzamide **6b**.—Compound **6b** was prepared by the reaction of **4b** (800 mg, 2.23 mmol) with benzoyl chloride (4.20 mg, 3.0 mmol) in the same manner as described above. Yield: 890 mg (86%); $[\alpha]_D^{20}$ +94.2 (*c* 1, CH_2Cl_2); λ_{max}(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 3380); ν_{max}(neat)/cm^{-1} 1630 (C=O); $\delta_H(CDCl_3)$ 0.28 (3H, s, Si-CH_3), 0.23 (3H, s, Si-CH_3), 0.056 (3H, s, Si-CH_3), 0.067 (3H, s, Si-CH_3), 0.73 [9H, s, Si-C$(CH_3)_3$], 0.91 [9H, s, Si-C$(CH_3)_3$], 1.95–2.30 (4H, m, CH_2), 3.06–3.14 (2H, m), 3.74 (1H, dd, *J* 9.8, 3.0), 3.84 (1H, dd, *J* 9.8, 5.4), 3.95 (m, 1H), 4.30–4.38 (m, 1H), 7.30–7.42 (m, 2H, Ar), 7.42–7.46 (m, 2H, Ar); *m*/*z* (FAB) 464 (M^+ + 1) (Found: C, 64.66; H, 9.79; N, 2.98. Calc. for $C_{25}H_{45}NSi_2O_3$: C, 64.74; H, 9.78; N, 3.02%).

Phthalamide **7b**.—Compound **7b** was prepared by the reaction of **4b** (700 mg, 1.95 mmol) with phthaloyl chloride (198 mg, 0.97 mmol) in the same manner as described above. Yield: 500 mg (61%); $[\alpha]_D^{20}$ +107.8 (*c* 1, CH_2Cl_2); mp 130–132 °C; λ_{max}-(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 5620); ν_{max}(KBr)/cm^{-1} 1630 (C=O); $\delta_H(CDCl_3)$ 0.36 (6H, s, Si-CH_3), 0.29 (6H, s, Si-CH_3), 0.035 (12H, s, Si-CH_3), 0.68 [18H, s, Si-C$(CH_3)_3$], 0.91 [18H, s, Si-C$(CH_3)_3$], 1.92–2.20 (8H, m, CH_2), 3.20 (2H, t, *J* 10.2), 3.56 (4H, m), 3.82 (2H, m), 3.92–4.0 (2H, m), 4.20–4.28 (2H, m), 7.30–7.42 (4H, m, Ar); *m*/*z* (FAB) 849 (M^+ + 1) (Found: C, 62.16; H, 9.99; N, 3.29. Calc. for $C_{44}H_{84}N_2Si_4O_6$: C, 62.21; H, 9.97; N, 3.30%).

Pyromellitamide **9b**.—Compound **9b** was prepared by the reaction of **4b** (1.45 mg, 4.04 mmol) with the corresponding acid chloride (0.33 g, 1.01 mmol) in benzene in the same manner as described above. Yield: 550 mg (34%); $[\alpha]_D^{20}$ +141.8 (*c* 1, CH_2Cl_2); mp 121–123 °C; λ_{max}(hexane)/nm 254 (ε/dm^3 mol^{-1} cm^{-1} 10 000); ν_{max}(KBr)/cm^{-1} 1630 (C=O); $\delta_H(CDCl_3)$ 0.12 (12H, s, Si-CH_3), 0.072 (12H, s, Si-CH_3), 0.061 (12H, s, Si-CH_3), 0.069 (12H, s, Si-CH_3), 0.82 [36H, s, Si-C$(CH_3)_3$], 0.91 [36H, s, Si-C$(CH_3)_3$], 1.92–2.20 (16H, m, CH_2), 3.20–3.30 (4H, m), 3.32–3.90 (12H, m), 3.92–4.0 (4H, m), 4.20–4.32 (4H, m), 7.32 (2H, s, Ar); *m*/*z* (FAB) 1621 (M^+ + 1) (Found: C, 60.39; H, 10.01; N, 3.39. Calc. for $C_{82}H_{162}N_4Si_8O_{12}$: C, 60.76; H, 10.07; N, 3.47%).

Benzamide **6c**.—Compound **6c** was prepared by the reaction of **4c** (200 mg, 0.45 mmol) with benzoyl chloride (70 mg, 0.5 mmol) in the same manner as described above. Yield: 195 mg (79%); $[\alpha]_D^{20}$ +71.6 (*c* 0.72, CH_2Cl_2); λ_{max}(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 3000); ν_{max}(neat)/cm^{-1} 1630 (C=O); δ_H($CDCl_3$) 0.84 (9H, d, *J* 5.4), 0.88 (9H, d, *J* 5.4), 1.054 (18H, s), 1.09 (6H, sept, *J* 5.4), 1.95–2.30 (4H, m, CH_2), 3.16–3.22 (2H, m), 3.88 (1H, dd, *J* 9.8, 3.0), 3.94 (1H, dd, *J* 9.8, 5.4), 4.0–4.10 (1H, m), 4.38–4.43 (1H, m), 7.30–7.40 (2H, m, Ar), 7.42–7.46 (3H, m, Ar); *m*/*z* (FAB) 548 (M^+ + 1) (Found: C, 67.91; H, 10.49; N, 2.56. Calc. for $C_{31}H_{57}NSi_2O_3$: C, 67.95; H, 10.49; N, 2.56%).

Phthalamide **7c**.—Compound **7c** was prepared by the reaction of **4c** (300 mg, 0.68 mmol) with phthaloyl chloride (69 mg, 0.34 mmol) in the same manner as described above. Yield: 210 mg (61%); mp 115–118 °C; $[\alpha]_D^{20}$ +78.5 (*c* 0.45, CH_2Cl_2); λ_{max}(hexane)/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 5630); ν_{max}(KBr)/cm^{-1} 1630 (C=O); δ_H($CDCl_3$) 0.84 (18H, d, *J* 5.4), 0.88 (18H, d, *J* 5.4), 1.054 (36H, s), 1.09 (12H, sept, *J* 5.4), 1.95–2.30 (8H, m, CH_2), 3.26 (2H, t, *J* 10.8), 3.60–3.78 (4H, m), 3.94–4.02 (2H, m), 4.10–4.20 (2H, m), 4.28–4.35 (2H, m), 7.30–7.42 (2H, m, Ar), 7.42–7.46 (2H, m, Ar); *m*/*z* (FAB) 1017 (M^+ + 1) (Found: C, 66.33; H, 10.64; N, 2.51. Calc. for $C_{56}H_{108}N_2Si_4O_6$: C, 66.08; H, 10.70; N, 2.75%).

Terephthalamide **8c**.—Compound **8c** was prepared by the reaction of **4c** (300 mg, 0.68 mmol) with terephthaloyl chloride (69 mg, 0.34 mmol) in the same manner as described above. Yield: 170 mg (50%); mp 129–131 °C; $[\alpha]_D^{20}$ +79.7 (*c* 0.60, CH_2Cl_2); λ_{max}(hexane)/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 5580); ν_{max}(KBr)/cm^{-1} 1630 (C=O); δ_H($CDCl_3$) 0.84 (18H, d, *J* 5.4), 0.88 (18H, d, *J* 5.4), 1.054 (36H, s), 1.09 (12H, sept, *J* 5.4), 1.95–2.32 (8H, m, CH_2), 3.25 (4H, d, *J* 5.4), 3.84 (2H, dd, *J* 9.5, 3.0), 4.00 (4H, dd, *J* 10.0, 5.0), 4.35–4.43 (2H, m), 7.48 (4H, s, Ar); *m*/*z* (FAB) 1017 (M^+ + 1) (Found: C, 66.01; H, 10.58; N, 2.58. Calc. for $C_{56}H_{108}N_2Si_4O_6$: C, 66.08; H, 10.70; N, 2.75%).

Pyromellitamide **9c**.—Compound **9c** was prepared by the reaction of **4c** (600 mg, 1.36 mmol) with the corresponding acid chloride (112 g, 0.34 mmol) in benzene in the same manner as described above. Yield: 150 mg (34%); $[\alpha]_D^{20}$ +70.9 (*c* 1.1, CH_2Cl_2); λ_{max}(hexane)/nm 245 (ε/dm^3 mol^{-1} cm^{-1} 8010); ν_{max}(neat)/cm^{-1} 1630 (C=O); δ_H($CDCl_3$) 0.96 (72H, d, *J* 5.4), 1.05 (72H, s), 1.09 (24H, sept, *J* 5.4), 1.95–2.32 (16H, m, CH_2), 3.45–4.0 (4H, m), 4.35–4.43 (20H, m), 7.18 (2H, s, Ar); *m*/*z* (FAB) 1955 (M^+ + 1) (Found: C, 64.94; H, 10.71; N, 2.79. Calc. for $C_{106}H_{210}N_4Si_8O_{12}$: C, 65.04; H, 10.81; N, 2.86%).

References

1 H. Rau, *Chem. Rev.*, 1983, **83**, 535.
2 Y. Inoue, *Chem. Rev.*, 1992, **92**, 441.
3 (*a*) Y. Inoue, T. Yokoyama, N. Yamasaki and A. Tai, *J. Am. Chem. Soc.*, 1989, **111**, 6480; (*b*) Y. Inoue, N. Yamasaki, T. Yokoyama and A. Tai, *J. Org. Chem.*, 1992, **57**, 1332; (*c*) Y. Inoue, N. Yamasaki, T. Yokoyama and A. Tai, *J. Org. Chem.*, 1993, **58**, 1011; (*d*) Y. Inoue, H. Tsuneishi, T. Hakushi and A. Tai, *J. Am. Chem. Soc.*, 1997, **119**, 472.
4 J.-I. Kim and G. B. Schuster, *J. Am. Chem. Soc.*, 1990, **112**, 9635.
5 Y. Inoue, T. Okano, N. Yamasaki and A. Tai, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 718.
6 G. S. Hammond and R. S. Cole, *J. Am. Chem. Soc.*, 1965, **87**, 3256.
7 (*a*) J. K. Whitesell and S. W. Felman, *J. Org. Chem.*, 1977, **42**, 1663; (*b*) R. H. Schlessinger and E. J. Iwanowicz, *J. Org. Chem.*, 1986, **51**, 3070; (*c*) M. Shi, Y. Satoh, T. Makihara and Y. Masaki, *Tetrahedron: Asymmetry*, 1995, **6**, 2109; (*d*) J. K. Whitesell, *Chem. Rev.*, 1989, **89**, 1581.
8 Y. Yamamoto, J. Hoshino, Y. Fujimoto, J. Ohmoto and S. Sawada, *Synthesis*, 1993, **3**, 298.
9 (*a*) A. C. Cope and R. D. Bach, *Organic Syntheses*, Wiley, New York, 1973; Collect Vol. 5, p. 315; (*b*) Y. Inoue, S. Takamuku and H. Sakurai, *Synthesis* (*Stuttgart*), 1977, 111.

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