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Discotic liquid crystals of transition metal complexes. Part 32.[1] Synthesis and liquid-crystalline properties of doubledeckers and tripledeckers based on cerium complexes of bis- and tetrakis(3,4-dialkoxyphenyl)porphyrin†

Teruhisa Nakai, Kazue Ban, Kazuchika Ohta* and Mutsumi Kimura

Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, 386-8567 Ueda, Japan. E-mail: ko52517@giptc.shinshu-u.ac.jp

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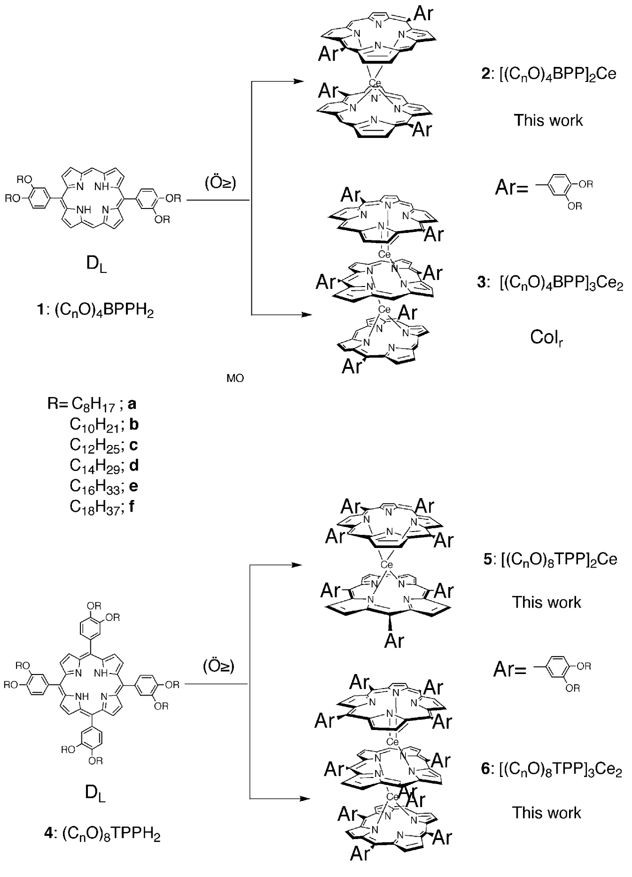
Novel sandwich-type doubledecker and tripledecker cerium complexes, bis[5,15-bis(3,4-dialkoxyphenyl)porphyrinato]cerium(IV) (**2**: $[(C_nO)_4BPP]_2Ce$; $n = 14$), bis[5,10,15,20-tetrakis(3,4-dialkoxyphenyl)porphyrinato]cerium(IV) (**5**: $[(C_nO)_8TPP]_2Ce$; $n = 8,10,12,14,16,18$), and tris[5,10,15,20-tetrakis(3,4-dialkoxyphenyl)porphyrinato]cerium(IV) (**6**: $[(C_nO)_8TPP]_3Ce_2$; $n = 10$), have been synthesized by using the corresponding metal free derivatives, 5,15-bis(3,4-dialkoxyphenyl)porphyrin (**1**: $(C_nO)_4BPPH_2$) and 5,10,15,20-tetrakis[3,4-bis(octadecyloxy)phenyl]porphyrins (**4**: $(C_nO)_8TPPH_2$) which were previously reported to show a discotic lamellar(D_L) mesophase. The mesophase structures of all these sandwich-type cerium complexes have been characterized in detail by microscopic observation, DSC measurements and temperature-dependent X-ray diffraction studies. We have investigated the critical molecular structure changing from lamellar mesophase-showing porphyrins to columnar mesophase-showing ones. We found that these sandwich-type multideckers may exhibit a columnar mesophase, when the central core is substituted by more than twelve alkoxy chains.

I. Introduction

Porphyrin and related compounds abound in various states in nature and function as a center of energy or carrier transport. For example, it is well known that the main electron-donor in the photosynthetic center of bacteria is the dimer of bacteria chlorophyll (Bchl) which is based on the porphyrin moiety.[2] In order to clarify the mechanism and apply its function as a center of energy, many porphyrin derivatives have been synthesized and investigated as a model biosystem.[3–5] Recently, dimers and oligomers of covalently-bonded porphyrins have been employed as novel photochemicals and molecular devices.[6–10] Thus, these porphyrin assemblies caused by aggregation and covalent bonds have great potential for application using their very unique and useful characteristics.

We have investigated discotic liquid crystals of π-electron macrocycles such as porphyrins and phthalocyanines substituted by alkoxy chains at the periphery. It is well known that these discotic liquid crystals tend to self-assemble and stack to show columnar(Col) and discotic-lamellar(D_L) mesophases. Previously, we reported that complexation of D_L-showing 5,15-bis[3,4-bis(dodecyloxy)phenyl]porphyrins **1c** with two cerium metal ions gave Col-showing tris[5,15-bis(3,4-didodecyloxyphenyl)porphyrinato]dicerium(III), **3c** derivatives (Scheme 1).[11,12] This means that rare earth metal porphyrin sandwiches can drastically change the mesomorphic structure from lamellar to columnar. The columnar structure is favorable to obtain higher electric conductivities. It is noteworthy that bis[octakis(dodecylthio)phthalocyaninato]lutetium(III) sandwich complex shows two columnar mesophases, one of which gives the highest mobility (0.7 $cm^2 V^{-1} s^{-1}$) in discotic liquid crystals reported so



Scheme 1 Synthetic route of $[(C_{14}O)_4BPP]_2Ce$, $[(C_nO)_8TPP]_2Ce$ ($n = 8,10,12,14,16,18$) and $[(C_nO)_8TPP]_3Ce_2$ ($n = 10,12$). (i) $Ce(acac)_3{\cdot}H_2O$–1,2,4-trichlorobenzene.

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†Electronic supplementary information (ESI) available: yields, elemental analysis data and electronic absorption spectral data. See http://www.rsc.org/suppdata/jm/b1/b109998c/

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far.[13] Thus, rare earth metal macrocycle sandwiches can be expected to be highly functional compounds.[14]

Accordingly, we are very interested in the critical molecular structure changing from lamellar-mesophase-showing porphyrins to columnar-mesophase-showing ones. However, there have been very few rare earth metal sandwiches in discotic liquid crystals investigated so far. The relationship between molecular shape and mesophase structure has never been studied for the sandwich complexes. Hence, in this work, we have synthesized the homologous 5,15-bis(3,4-dialkoxyphenyl)porphyrins (**1**, hereafter abbreviated as $(C_nO)_4BPPH_2$), the corresponding bis[5,15-bis(3,4-dialkoxyphenyl)porphyrinato]cerium(IV) (**2**, abbreviated as $[(C_nO)_4BPP]_2Ce$), and bis[5,10,15,20-tetrakis(3,4-dialkoxyphenyl)porphyrinato]cerium(IV) (**5**, abbreviated as $[(C_nO)_8TPP]_2Ce$) by using the corresponding metal free derivatives, **4**, abbreviated as $(C_nO)_8TPPH_2$, which were previously reported to show a discotic lamellar (D_L) mesophase. The mesophase structures of all these metal free derivatives and cerium(IV) sandwich complexes have been investigated in detail.

II. Results and discussion

II-1. Synthesis of multidecker cerium complexes

All the porphyrin derivatives investigated here are shown in Scheme 1. The metal free derivatives (**1** and **4**), bis(porphyrinato)cerium(IV) complexes(**2** and **5**) and tris(porphyrinato)dicerium(III) complexes (**3** and **6**) are hereafter called singledeckers, doubledeckers and tripledeckers, respectively. The detailed synthetic procedures will be presented in the Experimental section.

Fig. 1 shows separation of multideckers of the crude representative TPP derivatives by means of gel permeation chromatography (Bio-Beads SX-1, THF). The chain length did not affect the reactivity. As can be seen from this figure, a reaction time of 18.5 h gave a mixture of the unreacted singledecker **4e** and a small amount of the doubledecker **5e**. With a reaction time of 42 h a thicker colored band of the doubledecker **5e** was given, which apparently showed an increase in yield of **5e**. After 62.5 h, the tripledecker **6c** appeared. After about one week (207 h), the singledecker **4b** apparently decreased, and the doubledecker **5b** and the tripledecker increased. Thus, each of the yields of these multideckers based on TPP strongly depended on the reaction time. As previously reported, the BPP-based tripledecker, **3d**, $[(C_{14}O)_4BPP]_3Ce_2$, could be synthesized only for *ca.* 18 h.[12] On the other hand, the present TPP-based tripledecker, **6b**, $[(C_{10}O)_8TPP]_3Ce_2$, appeared after more than *ca.* 60 h. This is attributed to a greater steric hindrance of the four phenyl groups of TPP compared with the two phenyl groups of BPP, so that the complexation may take a much longer time.

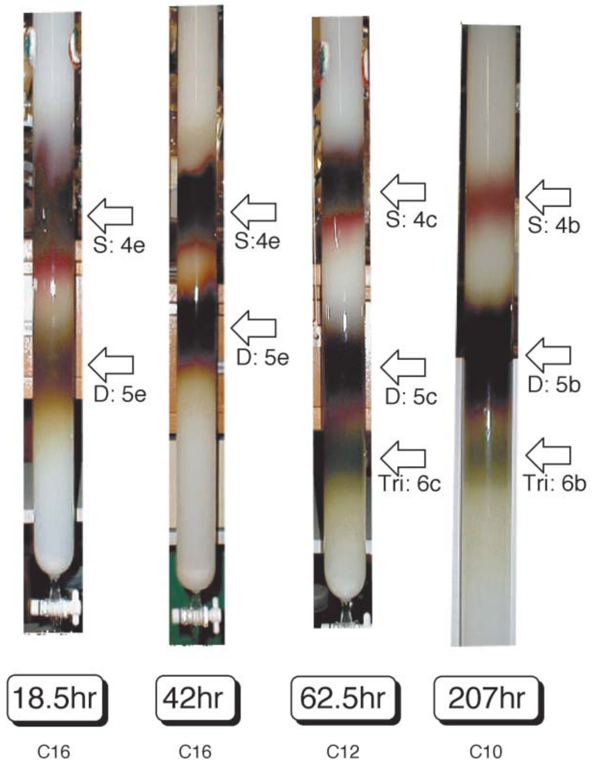

Fig. 1 Separation of multideckers from the crude TPP derivatives. S: Singledecker {**4** $(C_nO)_8TPPH_2$}; D: doubledecker {**5** $[(C_nO)_8TPP]_2Ce$}; Tri: tripledecker {**6** $[(C_nO)_8TPP]_3Ce_2$}.

Yields, elemental analysis data and mass spectral data of the porphyrin derivatives synthesized have been listed in Table S1†. Both **6b** ($[(C_{10}O)_8TPP]_3Ce_2$) and **6c** ($[(C_{12}O)_8TPP]_3Ce_2$) were produced in insufficient yields to be purified satisfactorily for the elemental analyses, but the observed masses were in good accord with the calculated ones (*e.g.*, Fig. 2).

II-2. UV-Vis spectra of the chloroform solutions

Figs. 3 and 4 illustrate spectra of the representative BPP and TPP derivatives, respectively. Each of the figures shows spectra of the singledecker, doubledecker and tripledecker from the top. Table S2† lists electronic absorption spectral data for the chloroform solutions of all the porphyrin derivatives investigated in this study. The singledeckers, **1** $[(C_nO)_4BPPH_2\{n = 10$ (**b**)–14 (**d**)$\}]$, show a Soret band and four Q bands characteristic to the metal-free porphyrins. The sandwich metal complexes show a Soret band and characteristic Q″, Q and Q′ bands. As can be seen from Fig. 3, the Soret bands are located at 412 nm for the singledecker **1d**, 388 nm for the doubledecker **2d**, and 399 nm for the tripledecker **3d**. Compared with the Soret band of the singledecker, those of the doubledecker and tripledecker blueshift by 24 nm and 13 nm, respectively. As can be seen from Fig. 4, the Soret bands of doubledecker **5b** and tripledecker **6b** also blueshift by 22 nm and 9 nm, respectively, compared with that of the singledecker. The blueshifts are very compatible with the results reported by Buchler *et al.*[15]

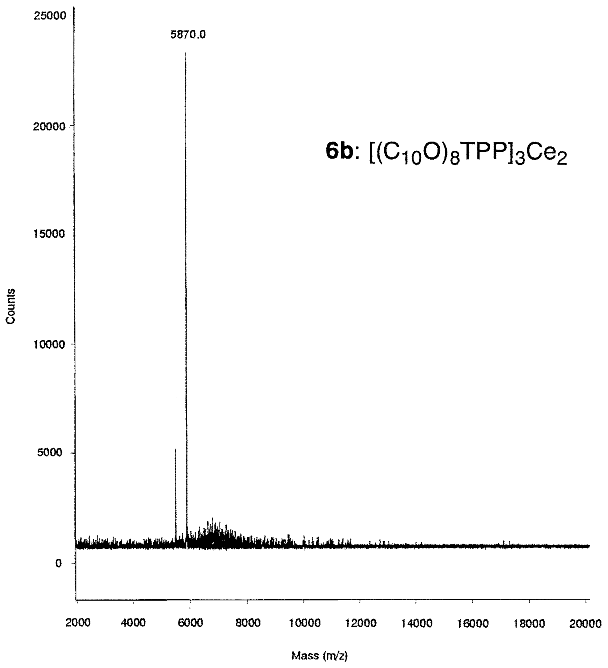

Fig. 2 MALDI-TOF Mass spectrum of **6b** ($[(C_{10}O)_8TPP]_3Ce_2$).

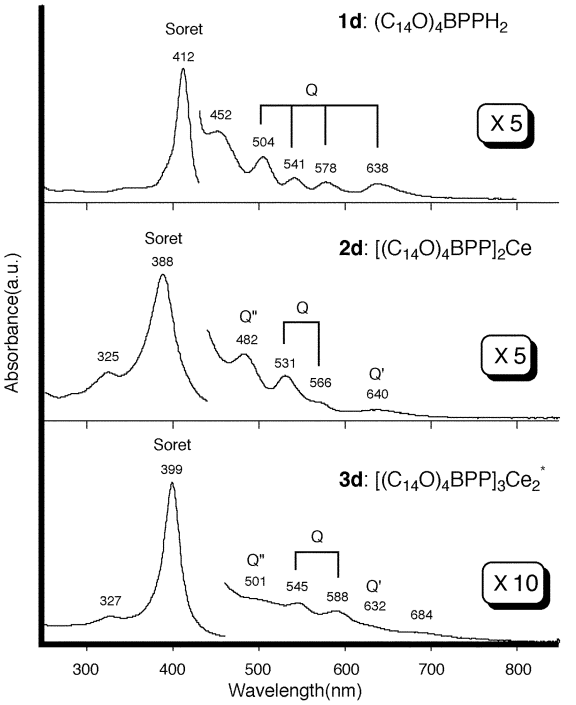

Fig. 3 Electronic spectra of the BPP derivatives in chloroform. The solution concentrations are listed in Table S2†. * Ref. 12.

II-3. Phase transition behaviour

Table 1 lists phase transition temperatures and enthalpy changes of the present porphyrin derivatives established by microscopic observation and DSC measurements.

As can be seen from this table, each of the singledecker **1** $(C_nO)_4BPPH_2$ {$n = 10$ (**b**)–14 (**d**)}, is crystalline at rt. When the freshly prepared (virgin) samples, **1b–d**, were heated by 10 °C min^{-1}, they melted into a discotic lamellar columnar (D_{LC}) mesophase at 91.5, 52.5 and 65.2 °C, respectively; then these D_{LC} mesophases cleared into isotropic liquid (I.L.) at 213.9, 200.7 and 182.6 °C, respectively. When the I.L. phase was cooled, they turned into the D_{LC} mesophase at the same temperatures as those clearing points. On further cooling, **1b** and **c** gave another crystalline phase.

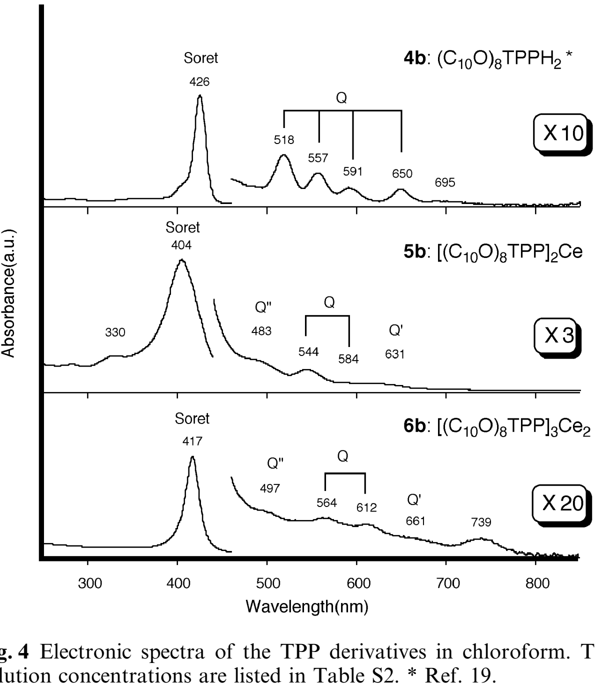

Fig. 4 Electronic spectra of the TPP derivatives in chloroform. The solution concentrations are listed in Table S2. * Ref. 19.

Table 1 Phase transition temperatures and enthalpy changes of $(C_nO)_4BPPH_2$ (n = 10, 12, 14), $[(C_{14}O)_4BPP]_2Ce$ (n = 14), $[(C_nO)_8TPP]_2Ce$ (n = 8, 10, 12, 14, 16, 18) and $[(C_nO)_8TPP]_3Ce_2$ (n = 10, 12)

Compound ; (n)		Phase	T/°C [ΔH/kJ mol^{-1}]	Phase	T/°C [ΔH/kJ mol^{-1}]	Phase
		K_{2V}	$\xrightarrow{91.5[68.0]}$	D_{LC}		
1: $(C_nO)_4BPPH_2$	**b**(10)	K_1	$\rightleftharpoons$ 33.8[35.6]	D_{LC}	$\rightleftharpoons$ 213.9[44.5]	I.L.
		X_V	$\xrightarrow{52.5}$	D_{LC}		
	c(12)^a	K	$\rightleftharpoons$ 60.4[55.6]	D_{LC}	$\rightleftharpoons$ 200.7[49.4]	I.L.
	d(14)	K	$\rightleftharpoons$ 65.2[18.6]	D_{LC}	$\rightleftharpoons$ 182.6[28.1]	I.L.
2: $[(C_nO)_4BPP]_2Ce$	**d**(14)	K	$\rightleftharpoons$ 93.3[27.9]	D_{LC}	$\rightleftharpoons$ 105.8[15.4]	I.L.
5: $[(C_nO)_8TPP]_2Ce$	**a**(8)			Col$_r$	$\rightleftharpoons$ 71.0[9.0] very slow	I.L.
	b(10)			Col$_r$	$\rightleftharpoons$ 70.3[12.0] very slow	I.L.
	c(12)					I.L. (r.t.)
	d(14)					I.L. (r.t.)
	e(16)			Col$_r$	$\rightleftharpoons$ 43.5[59.2] very slow	I.L.
	f(18)			Col$_r$	$\rightleftharpoons$ 51.3[85.5] very slow	I.L.
6: $[(C_nO)_8TPP]_3Ce_2$	**b**(10)					I.L. (r.t.)

^{a}Phase nomenclature: K: crystal, D_{LG}: discotic lamellar columnar mesophase, Col$_r$: rectangular columnar mesophase, I.L: isotropic liquid and X: unidentified phase. V means the virgin state. ^{b}Ref 19.

The doubledecker, **2d** ($[(C_{14}O)_4BPP]_2Ce$) is also crystalline at rt. When it was heated by 2.5 °C min^{-1}, it melted into a D_{LC} mesophase at 93.3 °C and cleared into I.L. at 105.8 °C. On cooling, these phases appeared again.

The doubledeckers, **5** ($[(C_nO)_8TPP]_2Ce$ {n = 8 (**a**), 10 (**b**), 16 (**e**), 18 (**f**)}), show a rectangular columnar(Col$_r$) mesophase at rt. When the doubledeckers, **5a**, **b**, **e**, and **f** were heated by 2.5 °C min^{-1}, they cleared into I.L. at 71.0, 70.3, 43.5 and 51.3 °C, respectively. Once they had cleared into I.L., they did not soon turn back to the original Col$_r$ mesophase. The non-virgin samples gave no peaks in the DSC measurements. These non-virgin samples were in a supercooled I.L. at rt. for several weeks. After three months, they gave the same DSC peaks as those of the virgin samples. Thus, the I.L. of these doubledeckers is too viscous to turn back to the Col$_r$ mesophase. The doubledeckers, **5c**, and **d**, are I.L. at rt. If these two derivatives were cooled down below rt., they might show a mesophase. However it would be impossible to determine the mesophase structures below 0 °C using our present X-ray instruments. Hence, such further investigations were not carried out.

The tripledecker, **6** ($[(C_nO)_8TPP]_3Ce_2$ {n = 10 (**b**)}) is also I.L. at rt, which was confirmed by polarizing microscopy.

Thus, the increase in the number of peripheral chains and complexation into the multideckers caused a decrease in the c.p.s. and a change from D_{LC} to Col$_r$.

II-4. Temperature-dependent X-ray diffraction studies

Table 2 summarizes the X-ray diffraction data of the mesophases of the porphyrin derivatives used in this study. The $(C_{10}O)_4BPPH_2$ singledecker, **1b**, at 150 °C gave three sharp

Table 2 X-Ray data of $(C_nO)_4BPPH_2$ (n = 10, 12, 14), $[(C_nO)_4BPP]_2Ce$ (n = 14) and $[(C_nO)_8TPP]_2Ce$ (n = 8, 10, 12, 14, 16, 18)

			Spacing			Phase
Compound	n	Peak no.	d_{obs}/Å	d_{calc}/Å	Miller indices (hkl)[a]	Lattice constant
1 $(C_nO)_4BPPH_2$	10 (**b**)	1	26.5	27.2	(001)	D_{LC} (= D_{L2})
		2	13.7	13.6	(002)	At 150 °C
		3	9.21	9.07	(003)	c = 27.2 Å
		4	*ca.* 6.5	—	h_2	h_2 = *ca.* 6.5 Å
		5	*ca.* 4.8	—	[b]	
	12 (**c**)[c]	1	30.9	30.6	(001)	D_{LC} (= D_{L2})
		2	15.2	15.3	(002)	At 125 °C
		3	10.2	10.2	(003)	c = 30.6 Å
		4	*ca.* 6.5	—	h_2	h_2 = *ca.* 6.5 Å
		5	*ca.* 4.8	—	[b]	
	14 (**d**)	1	33.1	33.5	(001)	D_{LC} (= D_{L2})
		2	16.9	16.8	(002)	At 150 °C
		3	11.2	11.2	(003)	c = 33.5 Å
		4	*ca.* 6.5	—	h_2	h_2 = *ca.* 6.5 Å
		5	*ca.* 4.7	—	[b]	
2 $[(C_nO)_4BPP]_2Ce$	14 (**d**	1	41.4	42.3	(001)	D_{LC} (= D_{L2})
		2	21.1	21.2	(002)	At 95 °C
		3	14.2	14.1	(003)	c = 42.3 Å
		4	*ca.* 8.6	—	h_2	h_2 = *ca.* 8.6 Å
		5	*ca.* 4.4	—	[b]	
		6	*ca.* 3.7	—	h_1	h_1 = *ca.* 3.7 Å
5 $[(C_nO)_8TPP]_2Ce$	8 (**a**)	1	28.8	28.8	(110)	Col_{rd} ($P2_1/a$)
		2	18.1	18.1	(120)	At rt
		3	13.1	13.1	(310)	a = 41.4 Å
		4	10.4	10.4	(400)	b = 40.2 Å
		5	9.32	9.21	(420)	
		6	7.95	7.89	(150)	
		7	6.92	6.91	(600)	
		8	6.17	6.14	(630)	
		9	*ca.* 4.2	—	[b]	
	10 (**b**)	1	31.1	30.5	(110)	Col_{rd} ($P2_1/a$)
		2	23.2	22.7	(200)	At rt
		3	18.7	18.7	(120)	a = 45.4 Å
		4	14.2	14.2	(310)	b = 41.0 Å
		5	13.1	13.1	(130)	
		6	11.3	11.3	(400)	
		7	10.6	10.9	(410)	
		8	8.84	8.86	(510)	
		9	8.07	8.08	(150)	
		10	6.40	6.41	(710)	
		11	*ca.* 4.2	—	[b]	
	12 (**c**)	—	—	—	—	I.L. at rt
	14 (**d**)	—	—	—	—	I.L. at rt
	16 (**e**)	1	31.1	—	—	X (= $Col_{rd}(P2_1/a)$) at rt
		2	*ca.* 4.2	—	[b]	
	18(**f**)	1	32.5	—	—	X (=$Col_{rd}(P2_1/a)$) at rt
		2	*ca.* 4.2	—	[b]	

[a] h_1: Intersingledecker distance h_2: interdoubledecker distance. [b] Halo of the molten alkoxy chains. [c] Ref. 19.

peaks in the angle region at 26.5, 13.7 and 9.21 Å, which are in a ratio of $1:\frac{1}{2}:\frac{1}{3}$, which is evidence of a lamellar structure. An additional peak at *ca.* 6.5 Å could be assigned to the stacking distance in the columnar structure corresponding to an interdimer distance (h_2). The porphyrins may form dimers in this mesophase. A broad halo located at *ca.* 4.8 Å corresponds to the molten alkoxy chains. From these facts this mesophase could be identified as a discotic lamellar columnar(D_{LC}) mesophase.[12] Similarly each of the other mesophases of **1c** and **b** could be identified as the same D_{LC} mesophase from the X-ray diffraction data at 125 °C and 150 °C, respectively.

The $[(C_{14}O)_4BPP]_2Ce$ doubledecker, **2d**, also showed a D_{LC} mesophase. Interestingly, this mesophase gave two stacking distances between doubledeckers at *ca.* 8.6 Å (h_2) and singledeckers at 3.7 Å (h_1). The stacking distance at 3.7 Å is attributed to rapid thermal fluctuations of the conformations of the disks which eliminates the crystallographic difference between the upper and lower disks in the doubledecker. If the difference was perfect, the stacking distance of *ca.* 3.7 Å (h_1) would not have been observed in the X-ray diffraction patterns. Thermal fluctuations may cause precession movements of the porphyrin disks. The imperfect precession movement may give a mixture of apparent singledeckers and doubledeckers on the time average to show these two stacking distances. The same phenomenon could be observed for the $[(C_{14}O)_8BPP]_3Ce_2$ tripledecker and $[(C_nS)_8Pc]_2M$ (M = Eu, Tb, Lu) sandwich complexes reported in our previous papers.[12,13]

X-Ray diffraction patterns of the $[(C_nO)_8TPP]_2Ce$ {**5**: n = 8 (**a**), 10 (**b**), 16 (**e**), 18 (**f**)} doubledeckers were obtained at rt. As can be seen from Fig. 5, the doubledeckers, **5a** and **b**, gave several peaks in the low angle region and a broad halo at 2θ = *ca.* 20°. The halo corresponds to the molten alkoxy chains. All the peaks in the low angle region could be assigned to reflections from a two-dimensional rectangular

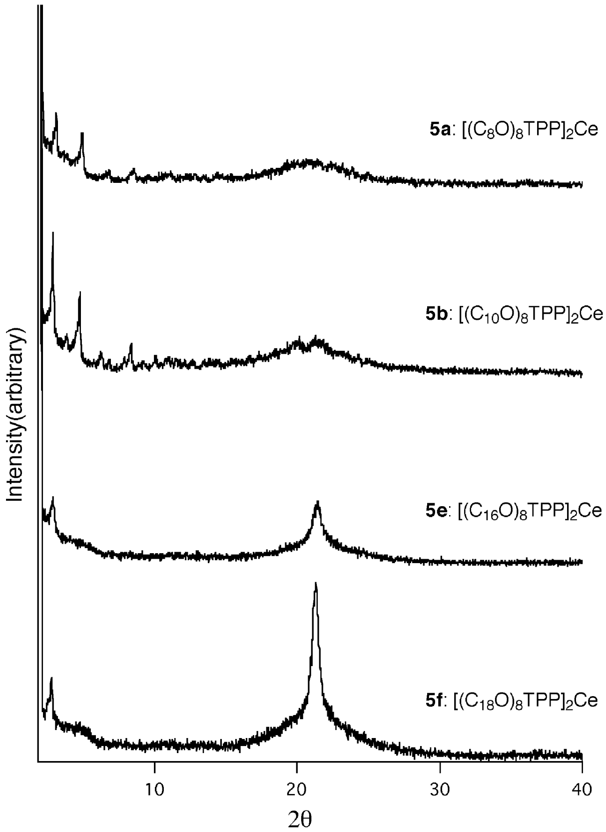

Fig. 5 X-Ray diffraction patterns of the $[(C_nO)_8TPP]_2Ce$ {**5**: **a** (n = 8), **b** (n = 10), **e** (n = 16), **f** (n = 18)} derivatives at rt.

lattice (Table 2). From the extinction rules for 2D-rectangular lattices,[16] it could be further assigned that the lattice has $P2_1/a$ symmetry. Interestingly, the mesophase did not give a peak corresponding to the stacking distance. Hence, this mesophase could be assigned as a disordered columnar mesophase, Col_{rd} ($P2_1/a$). As can be seen from Fig. 5, the other doubledeckers, **5e** and **f**, gave only one peak in the low angle region, which prevented us assigning these X mesophases. However, these mesophases can be also thought to be a Col_{rd} ($P2_1/a$) phase, because the mesophases may be the same in the other homologues even when the chain length becomes longer.

As can be seen from Fig. 5, the peaks at 2θ = *ca.* 20°, corresponding to the molten alkoxy chains, gradually change from a broad halo to a sharp one with increasing chain length. The same phenomenon was found by us for the D_L mesophases in $(C_nO)_8TPPH_2$ and $(C_nO)_8TPPCu$ in previous work.[17] We reported that these derivatives for n = 12 show complete melting of the alkoxy chains, whereas the longer-chain-substituted derivatives for n = 16 and 18 have two-dimensional hexagonal packing of the alkoxy chains in the D_L mesophases.[16] Accordingly, the present longer-chain-substituted derivatives, **5e** and **5f**, also have two-dimensional hexagonal packing of the alkoxy chains.

III. Conclusion

The BPP-based singledeckers (**1b–d**) and the corresponding cerium-containing doubledecker (**2d**), and the TPP-based cerium-containing doubledeckers (**5a–f**) and tripledeckers (**6b–c**) have been synthesized and their mesomorphism investigated .

The relationship between the molecular structures and their mesophase structures investigated here is summarized in Fig. 6. Among the BPP-based derivatives, the four and/or eight alkoxy-chain substituted singledeckers (**1**) and doubledecker (**2**) exhibit a discotic lamellar columnar (D_{LC}[12] = D_{L2}[18]) mesophase, whereas the twelve alkoxy-chain substituted tripledecker (**3d**) exhibits a rectangular columnar (Col_r) mesophase. Among the TPP-based derivatives, the eight alkoxy-chain substituted singledeckers (**4**) show a discotic lamellar (D_L = D_{L1})[18] mesophase, whereas the sixteen alkoxy-chain substituted doubledeckers (**5**) show a Col_r mesophase. Thus, the number of the alkoxy chains attached to the central core of a multidecker based on porphyrin disks may be a key point to the presence of the columnar mesophase. One can say that these sandwich-type of multideckers may exhibit a columnar mesophase, when the central core will be substituted by more than twelve alkoxy-chains. For the sandwich-type multideckers, the porphyrin disk units stack upon each other such that they may rotate by 20–45° thus avoiding the conflict of big phenyl groups. Thereby, when the porphyrin disk units are stacked up step by step such as singledecker → doubledecker → tripledecker, the peripheral space of the central core is gradually filled by alkoxy chains. Thus, the appropriate multidecker is a cylinder filled by flexible alkoxy chains in the periphery that shows columnar mesophase, Col_r character. This coincides with our previously reported result that a porphyrin disk was stepwise filled at the periphery with an increasing number of flexible alkoxy chains in order to change the mesomorphism from lamellar to columnar.[19]

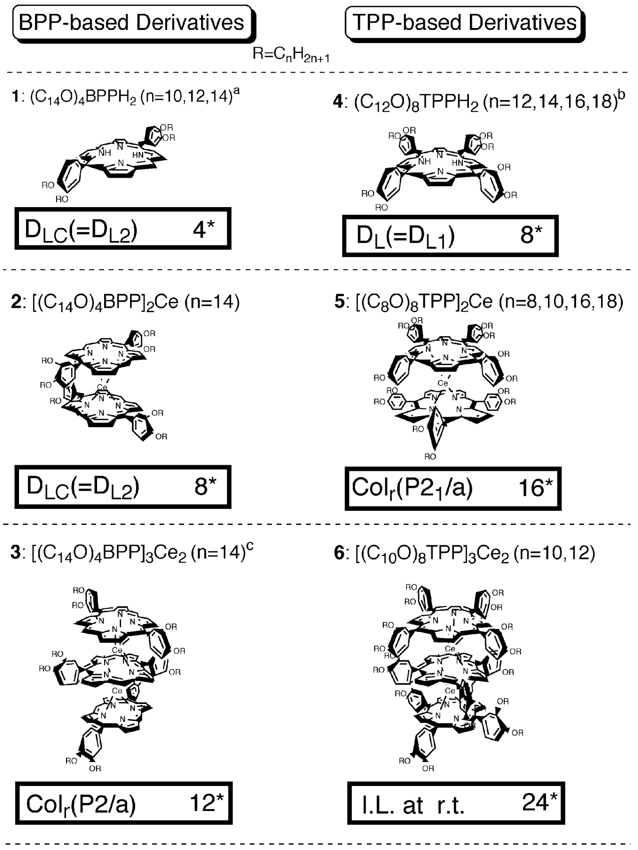

Fig. 6 The relationship between the molecular type of porphyrin derivatives and the resulting mesophase.

We believe that the relationship between the molecular and mesomorphic structures will be a good guideline to synthesize liquid crystalline porphyrin or phthalocyanine sandwich metal complexes.

IV. Experimental

IV-1. Synthesis

Scheme 1 shows the synthetic routes for all the porphyrin derivatives. The derivatives, **1b–d**, **3b–d** and **4**, have already been reported in our previous papers.[11,12,16,19] The metal free derivatives, **1** and **4** were prepared by the method of Adler *et al.*[20] The cerium-containing multideckers, **2**, **3**, **5** and **6**, were prepared by the method of Buchler *et al.*[15] and our previously reported procedures.[12]

5,15-Bis[3,4-bis(decyloxy)phenyl]porphyrin (1b). A mixture of 3, 4-bis(decyloxy)benzaldehyde (2.18 g, 5.2 mmol), 2,2′-dipyrromethane (0.75 g, 5.3 mmol) in 150 ml of dichloromethane and four drops of trifluoroacetic acid was stirred for 40 hours at room temperature. Then, to the reaction mixture *p*-chroranil (5.02 g, 20.4 mmol) was added, and the reaction mixture was refluxed for 3.5 hours. After removal of the solvent, the residue was purified by column chromatography (silica gel, chloroform $R_f = 1.00$) and recrystallized from acetone to give 0.23 g of **1b** as a purple solid. Yield 8%.

^{1}H-NMR ($CDCl_3$, TMS, ppm); −3.07 (broad, 2H, NH), 0.85 (t, 6H, CH_3, $J = 6$ Hz), 0.93 (t, 6H, CH_3, $J = 6$ Hz), 1.2–2.4 (m, 80H, $OCH_2(CH_2)_{10}CH_3$), 4.18 and 4.35 (t + t, 8H, OCH_2), 7.26–7.84 (m, 6H, ph), 9.15 and 9.38 (d + d, 8H, porphyrin), 10.3 (s, 2H, *meso*-H).

5,15-Bis[3,4-bis(tetradecyloxy)phenyl]porphyrin (1d). This compound was synthesized by a similar procedure to that described above. The crude product was purified by column chromatography (silica gel, chloroform $R_f = 1.00$) and recrystallized from acetone to give 0.08 g of **1d** as a purple solid. Yield 2%.

^{1}H-NMR ($CDCl_3$, TMS, ppm); −3.07 (broad, 2H, NH), 0.85 (t, 6H, CH_3, $J = 6$ Hz), 0.93 (t, 6H, CH_3, $J = 6$ Hz), 1.2–2.4 (m, 80H, $OCH_2(CH_2)_{10}CH_3$), 4.18 and 4.35 (t + t, 8H, OCH_2), 7.26–7.84 (m, 6H, ph), 9.15, and 9.38 (d + d, 8H, porphyrin), 10.3 (s, 2H, *meso*-H).

Bis{5,15-bis[3,4-bis(tetradecyloxy)phenyl]porphyrinato}cerium(IV) (2d). A mixture of 5,15-bis[3,4-bis(tetradecyloxy)phenyl]porphyrin (49.2 mg, 40.8 mmol) and cerium acetylacetonate (233 mg, 0.490 mmol) in 10 ml of 1,2,4-trichlorobenzene (TCB) was refluxed for 18 hours. TCB was distilled off under reduced pressure at 100 °C. Purification of the residue was carried out by column chromatography (neutral alumina gel; activity III, chloroform, $R_f = 1.00$). The multideckers were separated by permeation chromatography (Bio-beads gel SX-1, THF). The purities of the fractions was confirmed by electronic absorption spectroscopy. After removal of the solvent, the double-decker product was further purified by reprecipitation from ethyl acetate and acetone to afford 20.0 mg of brown powder. Yield 36%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1500 (ph), 1245 (ROPh).

The following cerium-containing multideckers (**5a–f**, **6b–c**, **7b**) were synthesized by a similar manner to that described above for **2d**.

Bis{5,10,15,20-tetrakis[3,4-bis(octyloxy)phenyl]porphyrinato}cerium(IV) (5a). The reaction time was 41 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 7 : 3, $R_f = 0.85$) and washed by acetone to give 88.6 mg as a dark brown solid. Yield 47%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1255 (ROPh).

Bis{5,10,15,20-tetrakis[3,4-bis(decyloxy)phenyl]porphyrinato}cerium(IV) (5b). The reaction time was 87 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 6 : 4, $R_f = 0.75$) and washed by acetone to give 71.1 mg as a dark brown solid. Yield 34%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1255 (ROPh).

Bis{5,10,15,20-tetrakis[3,4-bis(dodecyloxy)phenyl]porphyrinato}cerium(IV) (5c). This reaction time was 44 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 6 : 4, $R_f = 0.80$) and washed by acetone to give 152.4 mg as a black syrup. Yield 59%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1260 (ROPh).

Bis{5,10,15,20-tetrakis[3,4-bis(tetradecyloxy)phenyl]porphyrinato}cerium(IV) (5d). The reaction time was 43 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 5 : 5, $R_f = 0.85$) and washed by acetone to give 158.3 mg as a black syrup. Yield 62%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1255 (ROPh).

Bis{5,10,15,20-tetrakis[3,4-bis(hexadecyloxy)phenyl]porphyrinato}cerium(IV) (5e). The reaction time was 42 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 5 : 5, $R_f = 0.90$) and washed by acetone to give 75.5 mg as a black syrup. Yield 27%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1260 (ROPh).

Bis{5,10,15,20-tetrakis[3,4-bis(octadecyloxy)phenyl]porphyrinato}cerium(IV) (5f). The reaction time was 42 hours. After the multideckers had been separated by permeation chromatography (Bio-beads gel SX-1, THF), the target compound was purified by column chromatography (silica gel, toluene : *n*-hexane = 5 : 5, $R_f = 0.95$) and washed by acetone to give 23.2 mg as a black syrup. Yield 17%.

IR(KBr)/cm^{-1} 2925, 2850 (CH_2), 1510 (ph), 1255 (ROPh).

Tris{5,10,15,20-tetrakis[3,4-bis(decyloxy)phenyl]porphyrinato]dicerium(III) (6b). The reaction time was 207.5 hours. The multideckers were separated by permeation chromatography (Bio-beads gel SX-1, THF). The purities of the fractions was confirmed by electronic absorption spectroscopy. The second band afforded 2.4 mg as a black syrup. Yield 0.8%.

Tris{5,10,15,20-tetrakis[3,4-bis(dodecyloxy)phenyl]porphyrinato}dicerium(III) (6c). The reaction time was 87 hours. The multideckers were separated by permeation chromatography (Bio-beads gel SX-1,THF). The purities of the fractions were confirmed by electronic absorption spectroscopy. The first band afforded 11.2 mg of a black syrup. Yield 8%.

IV-2. Measurements

The products synthesized here were identified by ^{1}H-NMR (JOEL JNM-FX90A) and IR (Jasco A-100). Further identification of the porphyrin derivatives were made by MALDI-TOF mass analysis (PerSeptive Biosystems Voyager DE-Pro spectrometer), elemental analysis (Perkin-Elmer elemental analyzer 2400) and electronic absorption spectroscopy (Hitachi 330 spectrophotometer).

The phase transition behaviour of these compounds was observed by using a polarizing microscope (Olympus BH2), equipped with a heating plate controlled by a thermoregulator (Mettler FP80 hot stage, Mettler FP80 Central Processor), and measured by a differential scanning calorimeter (Shimadzu DSC-50). The X-ray diffraction measurements were performed with Cu-Kα radiation (Rigaku RAD) equipped with a hand-made heating plate[21] controlled by a themoregulator.

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References

1 Part 31: (*a*) H. Horie, A. Takagi, H. Hasebe, K. Ohta and I. Yamamoto, *J. Mater. Chem.*, 2001, **11**, 1063.

2 (*a*) M. S. Davis, A. Forman, L. K. Hanson, J. P. Thornber and J. Fajer, *J. Phys. Chem.*, 1979, **83**, 3325; (*b*) A. Warshel and W. W. Parson, *J. Am. Chem. Soc.*, 1987, **109**, 6147; (*c*) W. W. Parson and A. Warshel, *J. Am. Chem. Soc.*, 1987, **109**, 6152.

3 K. M. Smith and D. J. Simpson, *J. Am. Chem. Soc.*, 1987, **109**, 6326.

4 I. Constantinidis and J. D. Satterlee, *J. Am. Chem. Soc.*, 1988, **110**, 4391.

5 (*a*) J. P. Collman, A. O. Chong, G. B. Jameson, R. T. Oakley, E. Rose, E. R. Schmittou and J. A. Ibers, *J. Am. Chem. Soc.*, 1981, **103**, 516; (*b*) T. L. Netzel, M. A. Bergkamp and C. K. Chang, *J. Am. Chem. Soc.*, 1982, **104**, 1952; (*c*) J. H. Fuhrhop, E. Baumgartner and H. Bauer, *J. Am. Chem. Soc.*, 1981, **103**, 5854; (*d*) R. R. Bucks and S. G. Boxer, *J. Am. Chem. Soc.*, 1982, **104**, 340; (*e*) M. R. Wasielewski, W. A. Svec and B. T. Cope, *J. Am. Chem. Soc.*, 1978, **100**, 1961.

6 (*a*) A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, 1988, **110**, 4454; (*b*) T. Nagata, A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, 1990, **112**, 3054; (*c*) A. Osuka, S. Nakajima, K. Maruyama, N. Mataga and T. Asahi, *Chem. Lett.*, 1991, 1003; (*d*) A. Osuka and H. Shimidzu, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 135; (*e*) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono and A. Osuka, *Chem. Commun.*, 1998, 337; (*f*) T. Ogawa, Y. Nishimoto, N. Yoshida, N. Ono and A. Osuka, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 176.

7 M. J. Crossley, P. L. Burn, S. J. Langford and J. K. Prashar, *J. Chem. Soc., Chem. Commun.*, 1995, 1921.

8 H. Higuchi, K. Shimizu, M. Takeuchi, J. Ojima, K. Sugiura and Y. Sakata, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1923.

9 (*a*) M. Takeuchi, T. Imada and S. Shinkai, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1117; (*b*) A. Sugasaki, M. Ikeda, M. Takeuchi, A. Robertson and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 3259.

10 T. A. Vannelli and T. B. Karpishin, *Inorg. Chem.*, 1999, **38**, 2246.

11 K. Ban, Masters thesis. Shinshu University, Ueda, 1998, ch. 1.

12 H. Miwa, N. Kobayashi, K. Ban and K. Ohta, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2719.

13 (*a*) K. Ban, Masters thesis. Shinshu University, Ueda, 1998, ch. 4; (*b*) K. Ban, K. Nishizawa, K. Ohta, A. M. van de Craats, J. M. Warman, I. Yamamoto and H. Shirai, *J. Mater. Chem.*, 2001, **11**, 321.

14 (*a*) H. Tran-Thi, *Cood. Chem. Rev.*, 1997, **160**, 53; (*b*) J. H. Perng, J. K. Duchowski and D. F. Bocian, *J. Phys. Chem.*, 1990, **94**, 6684; (*c*) R. J. Donohoe, J. K. Duchowski and D. Bocian, *J. Am. Chem. Soc.*, 1988, **110**, 6119; (*d*) J. H. Perng, J. K. Duchowski and D. F. Bocian, *J. Phys. Chem.*, 1991, **95**, 1319; (*e*) X. Yan and D. Holten, *J. Phys. Chem*, 1988, **92**, 409; (*f*) O. Bilsel, J. Rodriguez, D. Holten, G. S. Girolami, S. N. Milam and K. S. Suslik, *J. Am. Chem. Soc.*, 1990, **112**, 4075; (*g*) O. Bilsel, J. Rodriguez, S. N. Milam, P. A. Gorlin, G. S. Girolami, K. S. Suslick and D. Holten, *J. Am. Chem. Soc.*, 1992, **114**, 6528; (*h*) O. Bilsel, S. N. Milam, G. S. Girolami, K. S. Suslick and D. Holten, *J. Phys. Chem*, 1993, **97**, 7216; (*i*) L. L. Wittmer and D. Holten, *J. Phys. Chem*, 1996, **100**, 860.

15 J. W. Buchler, A. D. Cian, J. Fischer, M. K. Botulinski, H. Paulus and R. Weiss, *J. Am. Chem. Soc.*, 1986, **108**, 3652; K. Ban, Masters thesis, Shinshu University, Ueda, 1998, ch. 1.

16 T. Komatsu, K. Ohta, T. Watanabe, H. Ikemoto, T. Fujimoto and I. Yamamoto, *J. Mater. Chem.*, 1994, **4**, 537.

17 K. Ohta, N. Ando and I. Yamamoto, *Liq. Cryst.*, 1999, **26**, 663.

18 K. Ohta, H. Muroki, A. Takagi, K. Ichihatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1986, **140**, 131.

19 K. Ohta, N. Yamaguchi and I. Yamamoto, *J. Mater. Chem.*, 1998, **8**, 2637.

20 D. Adler, F. R. Longo, J. D. Finareli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

21 H. Ema, Masters Thesis, Shinshu University, Ueda, Japan, 1988, ch. 7; H. Hasebe, Masters Thesis, Shinshu University, Ueda, Japan, 1991, ch. 5.