Metal Complexes with Tetrapyrrole Ligands, LXVI[1,2]

Synthesis, Characterization, and Variable-Temperature ^{1}H- and ^{19}F-NMR Investigations of Cerium(IV) Double-Deckers Derived from Monofunctionalized Tetraarylporphyrins

Johann W. Buchler*[a], Volker Eiermann[b], Helmut Hanssum[c], Georg Heinz[a], Heinz Rüterjans[c], and Markus Schwarzkopf[b]

Institut für Anorganische Chemie, Technische Hochschule Darmstadt[a],
Hochschulstraße 10, D-64289 Darmstadt, Germany

E. Merck, Central Analytical Laboratory[b],
Frankfurter Straße 250, D-64271 Darmstadt, Germany

Institut für Biophysikalische Chemie der Universität Frankfurt[c], Universitäts-Klinikum, Haus 75a,
D-60590 Frankfurt am Main, Germany

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The synthesis of a cerium(IV) bisporphyrinate **1b** starting from (*p*-hydroxyphenyl)tris(*p*-tolyl)porphyrin **2b** is described. Derived from **2b** by substitution of the phenolic OH group, the monofunctionalized tetraarylporphyrins **2c–f** and their cerium(IV) sandwich complexes **1c–f** were synthesized. The complexes are characterized by UV/Vis, IR, and ^{1}H-NMR spectroscopy. ^{19}F-NMR spectra of **1f** show the presence of a vicinal and a transversal isomer due to the rigid square-antiprismatic coordination geometry of cerium(IV) bisporphyrinates. Variable-temperature ^{1}H- and ^{19}F-NMR spectra were recorded to investigate the rotational rigidity of the double-decker system. The spectra show that the vicinal and transversal isomers are stable up to 140°C, i.e. rotation of the two porphyrin macrocycles with respect to each other does not occur.

Porphyrin sandwich complexes $M(P)_2$[3] with tetravalent metal ions are known for several years. Since the preparation of the first porphyrin sandwich complex $Ce(TTP)_2$[4] **1a** the synthesis of uranium and thorium[5] as well as zirconium and hafnium bisporphyrinates[6,7] has been reported. These sandwich systems can be regarded as structural and spectroscopic models[8] of the special pair of bacteriochlorophyll molecules in the reaction centre of bacterial photosynthesis[9].

All available crystal structures indicate a square antiprismatic coordination geometry of sandwich-like metal bisporphyrinates[10] in the solid state. In principle, metal bisporphyrinates with the coordination number 8 could exist in solution as isomers with cubic or dodecahedral coordination geometry as well or as mixtures of these isomers if there is freedom of motion of the two porphyrin ligands against each other. In order to distinguish between different kinds of isomers, it is necessary to choose porphyrin ligands which have lower symmetry than common tetraaryl- and octaalkylporphyrins which give a D_{4d} symmetry to the respective metal bisporphyrinates $M(P)_2$. NMR techniques should be useful to determine the conformation(s) of double-deckers in solution when the porphyrin ligands are monofunctionalized. If the square antiprismatic coordination geometry is predominant in solution, there should be two isomers with C_2 symmetry in monofunctionalized tetraarylporphyrins. In each isomer, the two monofunctionalized aryl groups are equivalent (C_2 axis). This is exemplified in Scheme 1.

Additionally, variable-temperature NMR measurements should allow investigation of the rotational rigidity of the double-decker system, i.e. whether rotation of the the two porphyrin macrocycles with respect to each other occurs.

Here, the preparation of cerium sandwich complexes **1b–f** of (*p*-hydroxyphenyl)tris(*p*-tolyl)porphyrin[11] **2b** and its derivatives **2c–f** is performed by using well-known methods for the insertion of cerium into porphyrins with $Ce(acac)_3$[12] in 1,2,4-trichlorobenzene (TCB) to obtain diamagnetic sandwich complexes suitable for NMR investigations.

Results and Discussion

Cerium insertion with $Ce(acac)_3$ in Li_2(LiOTTP) [prepared in situ from H_2(HOTTP) and *n*-butyllithium] yielded pure $Ce(HOTTP)_2$ (**1b**) [eq. (1), P^{2-} = $(HOTTP)^{2-}$] after chromatographic workup.

$$Ce(acac)_3 \xrightarrow[\substack{-3\ Li(acac),\ -Li^+,\ -e^- \\ (TCB,\ 200°C)}]{2\ Li_2(P)} Ce(P)_2 \qquad (1)$$

But this compound is not suitable for detecting isomers by NMR investigations. The OH proton signal (s, δ = 5.07) of the compound does not show any splitting over the

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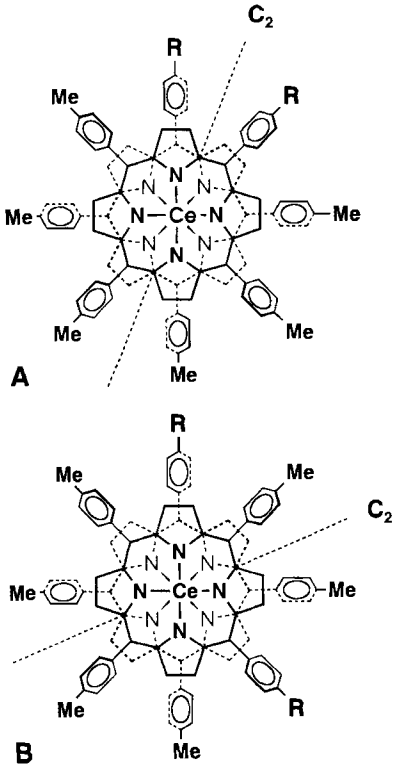
Scheme 1. **A**: vicinal, **B**: transversal isomer of the bis[5-(4-substituted-phenyl)-10,15,20-tris(*p*-tolyl)porphyrinato]cerium(IV) complexes. For the metal-free porphyrins, see Scheme 2. C_2 in **A** or **B** indicates the two-fold symmetry axes of the molecules

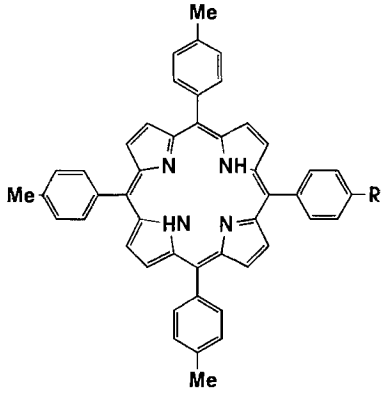


Specification of the double-deckers 1a-1f

No.	R in A,B	Short formula
1a	CH_3	$Ce(TTP)_2$
1b	OH	$Ce(HOTTP)_2$
1c	OMe	$Ce(MeOTTP)_2$
1d	$OCOC_6H_5$	$Ce(BzOTTP)_2$
1e	$OCOC_6H_4CH_3$	$Ce(TuOTTP)_2$
1f	$OCOC_6F_5$	$Ce(PfOTTP)_2$

whole range of temperatures between 233 and 373 K. The pyrrole signals (between δ = 8.24 and 8.33, Table 1) are quite complex and not helpful to determine isomers. All the other aryl-H signals of the compound are broad at 323 K and collapse to one signal between 323 and 348 K. Similar observations have been made with $Zr(TPP)_2$[13]. At lower temperatures (between 233 and 298 K) signals of the tolyl groups and the hydroxyphenyl group can be distinguished, but signals of different tolyl or hydroxyphenyl groups are not seen. Hence aryl- and pyrrole-H atom signals are both not feasible to determine isomers at low temperature and not at all at high temperature.

Scheme 2. Specification of the free porphyrins



No.	R	Short formula
2a	CH_3	$H_2(TTP)$
2b	OH	$H_2(HOTTP)$
2c	OMe	$H_2(MeOTTP)$
2d	$OCOC_6H_5$	$H_2(BzOTTP)$
2e	$OCOC_6H_4CH_3$	$H_2(TuOTTP)$
2f	$OCOC_6F_5$	$H_2(PfOTTP)$

The possibility remained that proton signals of functional groups attached to the two phenolic oxygen atoms in $Ce(HOTTP)_2$ might display the presence of isomers like **A** and **B**. Simply replacing the H atom of $H_2(HOTTP)$ with methyl iodide (eq. 2) yielded the porphyrin $H_2(MeOTTP)$ (**2c**) which can be metallated according to eq. (1) [P^{2-} = $(MeOTTP)^{2-}$] to obtain the new double-decker $Ce(MeOTTP)_2$ (**1c**). Unfortunately, the proton signal of the OMe group of this compound appears as a singlet (δ = 4.10) between 233 and 373 K.

$$MeI + H_2(HOTTP) \xrightarrow[\text{(toluene, 40°C)}]{\text{NaOEt}} H_2(MeOTTP) \quad (2)$$

Acylation of the phenolic hydroxyl group of $H_2(HOTTP)$ with acyl chlorides such as benzoyl chloride and *p*-toluyl chloride [eq. (3), R = C_6H_5CO and $CH_3C_6H_4CO$] produced the porphyrins $H_2(BzOTTP)$ (**2d**) and $H_2(TuOTTP)$ (**2e**).

$$H_2(HOTTP) + RCl \xrightarrow[\text{(}CHCl_3\text{, room temp.)}]{\text{Py}} H_2(ROTTP) \quad (3)$$

However, metal insertion into these porphyrins failed[14]. Under the reaction conditions (boiling TCB, basic medium) hydrolysis of the ester functions occured. In both cases the double-decker $Ce(HOTTP)_2$ was obtained after workup.

Therefore, $Ce(HOTTP)_2$ was choosen as the starting compound for the acylation reaction [eq. (4), R = C_6H_5CO and $CH_3C_6H_4CO$] although as a side reaction some demet-

allation occurs due to the sensitivity of cerium sandwich complexes towards acids. However, with this method, the new double-deckers $Ce(BzOTTP)_2$ (**1d**) and $Ce(TuOTTP)_2$ (**1e**) were obtained. The ^{1}H-NMR spectra of these compounds are both more helpful to demonstrate the presence of isomers because at temperatures below 273 K quite complex signals of the protons of the oxyphenyl group are observed.

$$Ce(HOTTP)_2 + RCl \xrightarrow[-\,[PyH]Cl]{Py} Ce(ROTTP)_2 \quad (4)$$
($CHCl_3$, room temp.)

Finally, the cerium bisporphyrinate $Ce(PfOTTP)_2$ (**1f**) was prepared [according to eq. (4) with pentafluorobenzoyl chloride, R = C_6F_5CO]. This compound has the advantage that not only ^{1}H-NMR but also ^{19}F-NMR data can be discussed which are more useful at higher temperatures than the ^{1}H-NMR spectra (collapse of all aryl-H atom signals above 348 K). Taking into account that ^{19}F nuclei are quite sensitive to their chemical sourroundings[15], ^{19}F-NMR techniques should be a very powerful tool to detect isomers.

Analytical and Spectral Characterization of the Cerium(IV) Complexes

All new complexes gave correct microanalyses and molecular ions (detected as doubly charged molecular ions) in the mass spectra. The individual porphyrin system in the double deckers can be identified by both IR and ^{1}H-NMR spectra. The former show the characteristic C–H and skeletal vibrations of the ligands and also the vibration of the individual functional group. The ^{1}H-NMR signals of the double-deckers are given in Table 1. UV/Vis data of the new sandwich complexes do not differ from spectra which are known from the reference compound $Ce(TTP)_2$[4] and are presented in the Experimental Part.

^{1}H- and ^{19}F-NMR Spectra of $Ce(PfOTTP)_2$ at Variable Temperatures

In agreement with ^{1}H-NMR spectra of cerium bistetraarylporphyrinates[5] a splitting of *ortho* and *meta* proton signals in a set of *exo* and *endo* signals (Figure 1 and Table 1) is found due to the diastereotopic property of these aryl protons. The proton signals of the oxyphenyl group and the tolyl group, respectively, are separated. The higher resolution of the aryl-H signals at lower temperature (Figure 1) is due to the decreasing mobility of the aryl groups[13,16]. The multiplets of the oxyphenyl signals (*ortho* signals: δ = 9.67 and 6.52, *meta* signals: δ = 8.04 and 7.15) are quite complex [*o*- and *m*-H atoms of $Zr(TPP)_2$ show doublets at low temperature[13]] and could be interpreted as a superposition of signals of two isomers although there is incomplete separation of the signals.

The spectra taken at higher temperatures (Figure 2) show increasing mobility of the aryl groups. At 323 K the signals of the aryl protons are broad. Thus, no distinction can be made between tolyl and oxyphenyl signals. Free rotation of the aryl groups about the C–C bond to the *meso*-C atom of the porphyrin is indicated by the collapse of all aryl-H atom signals at 348 K and higher temperatures.

The different pattern of the ^{19}F resonance signals of the *p*-F atoms of the free porphyrin and the double-decker shows the presence of isomers in the latter case (Figure 3). Due to the C_2 symmetry of the complexes (equivalence of the functionalized aryl group in each isomer) and the free rotation of the pentafluorobenzoyl groups about the ester bonds, only one set of *o*-, *m*-, and *p*-F atoms occurs in each isomer. If there would be only one isomer the same lineshape as observed with the free porphyrin should be observed. In agreement with this finding the signals of the *o*- and *m*-F atoms of the double-decker are different from those of the free porphyrin as well and more complex [H_2(PfOTTP): *o*-F, δ = −136.87 to −137.06 (m), *m*-F, −159.91 to −160.16 (m); $Ce(PfOTTP)_2$: *o*-F, −136.88 to −137.08 (m), *m*-F, −159.90 to −160.15 (m)][15]. The shape of the signal caused by the *p*-F atom of the double-decker can be explained by a superposition of the *p*-F signals separated with 4.4 Hz (0.016 ppm) of two double-decker isomers present in a 1:1 ratio.

To simplify the interpretation of the ^{19}F-NMR spectra at various temperatures only the signal of the *p*-F atom in the pentafluorobenzoyl group is considered (Figure 4). The ^{19}F-NMR spectra of the double-decker indicate that the conformations of the isomers are quite stable up to 373 K and that rotation of the two porphyrin ligands with respect to each other does not occur up to 413 K (boiling point of $C_2D_2Cl_4$). The broad signals between 373 and 413 K indicate an increasing movement of the two porphyrin macrocycles with respect to each other but by no means free rotation of the ligands. After cooling down the solution from 413 to 303 K a ^{19}F-NMR spectrum was recorded with signals of the same shape and intensity as obtained before heating at this temperature. Thus, isomerization to a mixture of different isomer distribution does not occur up to 413 K.

The synthesis of **1b** is done at about 500 K. Free rotation of the two porphyrin rings may occur at this elevated temperature. On cooling the reaction mixture, the two isomers corresponding to **A** and **B** (Scheme 1) will form in a 1:1 molar ratio due to the very small energy difference which is to be expected for **A** and **B**. Thus, the observed 1:1 ratio seems plausible.

Conclusion

Cerium sandwich complexes with monofunctionalized tetraarylporphyrins exist as a mixture of a vicinal and a transversal isomer with a quite stable square antiprismatic coordination geometry (Scheme 1). This is prooved for **1f** and assumed for **1b–e**. The square antiprismatic environment of the metal minimizes the steric interactions of the two porphyrin ligands and prevents strong steric interactions between the *meso*-phenyl groups of the two tetraarylporphyrins as they would exist for example in tetraarylporphyrin sandwich complexes with cubic or dodecahedral coordination geometry. Unfortunately, due to the very similar chemical and physical properties of the isomers, it was not

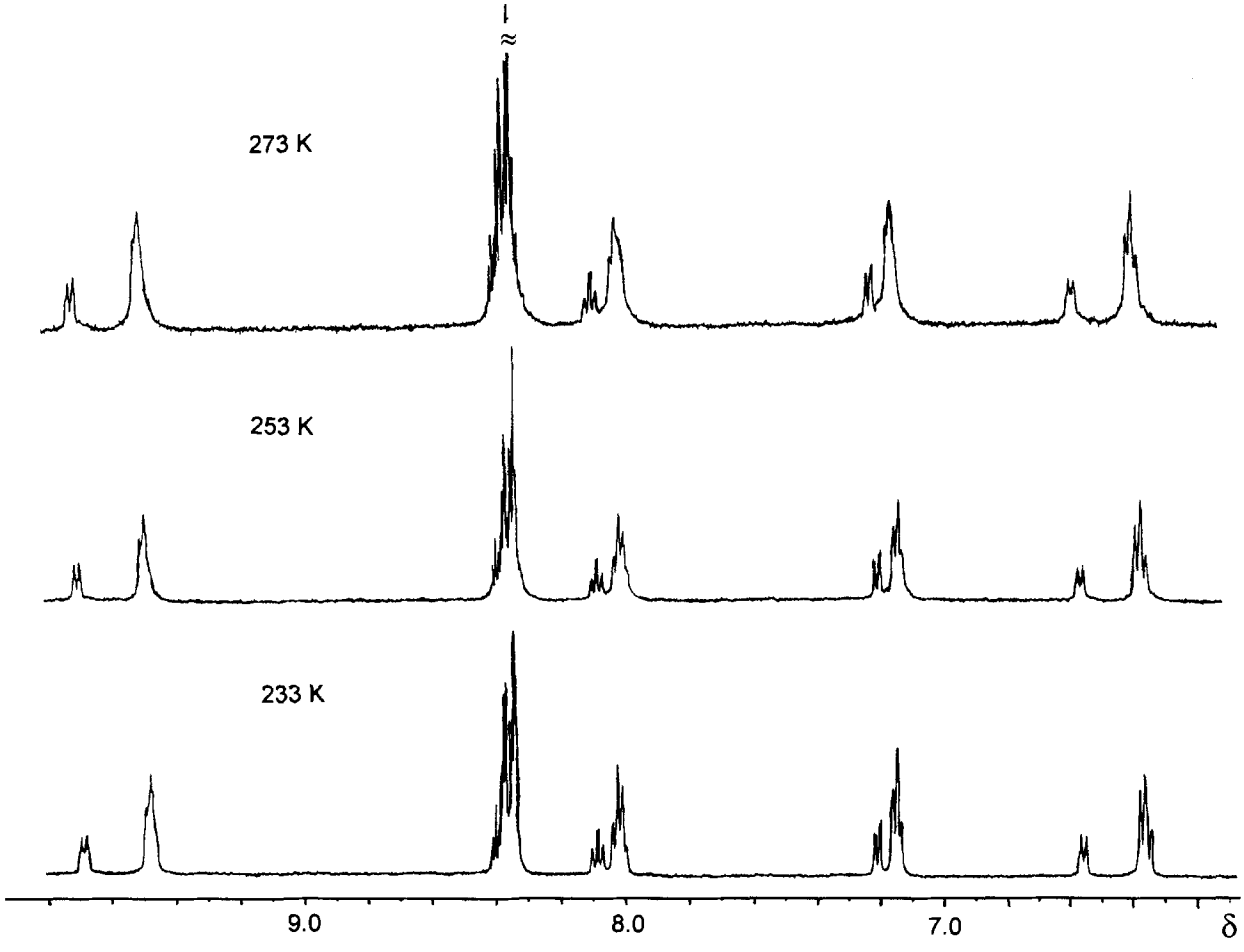


Figure 1. Temperature dependence of the ^{1}H-NMR spectra of Ce(PfOTTP)$_2$ ($CDCl_3$, δ scale, int. TMS, 500 MHz)

Table 1. ^{1}H-NMR data of the cerium bisporphyrinates **1b–f** (δ values, int. TMS, 300 MHz, in CD_2Cl_2, 298 K)

	Pyrrole H	*p*-Tolyl groups					*p*-Oxyphenyl groups				*p*-Oxy substituents
		o-H	*o'*-H	*m*-H	*m'*-H	CH_3	*o*-H	*o'*-H	*m*-H	*m'*-H	
1b	8.24-8.33	9.44	6.33	7.94	7.09	2.71	9.44	6.33	7.61	6.77	OH: 5.07 (s)
	m	m	m	m	m	m	m	m	m	m	
1c	8.21-8.35	9.45	6.34	7.95	7.10	2.72	9.45	6.34	7.65	6.83	OCH_3: 4.10 (s)
	m	m	m	m	m	m	m	m	m	m	
1d	8.22-8.42	9.45	6.33	7.94	7.10	2.71	9.65	6.50	7.94	7.10	benzoyl: 8.39 (m, 2,6-H), 7.66
	m	m	m	m	m	m	m	m	m	m	(m, 3,5-H), 7.75 (m, 4H)
1e	8.29-8.35	9.46	6.34	7.96	7.12	2.72	9.63	6.51	7.96	7.12	*p*-toluyl: 8.35 (m, 2,6-H), 7.46
	m	m	m	m	m	m	m	m	m	m	(m, 3,5-H), 2.53 (s, CH_3)
1f	8.22-8.39	9.46	6.36	8.01	7.13	2.72	9.67	6.52	8.04	7.15	
	m	m	m	m	m	m	m	m	m	m	

possible to separate the two isomers with column or thin layer chromatography. Attempts to solve this problem with HPLC techniques are in progress.

Recently, the synthesis of monofunctionalized zirconium bisporphyrinates[17] has been reported. Details are not given, but NMR investigations of these zirconium sandwich complexes show that rotation of the porphyrin ligands with respect to each other does not occur up to 423 K. In agreement with our findings the square antiprismatic coordination geometry is quite stable in zirconium porphyrin sandwich complexes as well.

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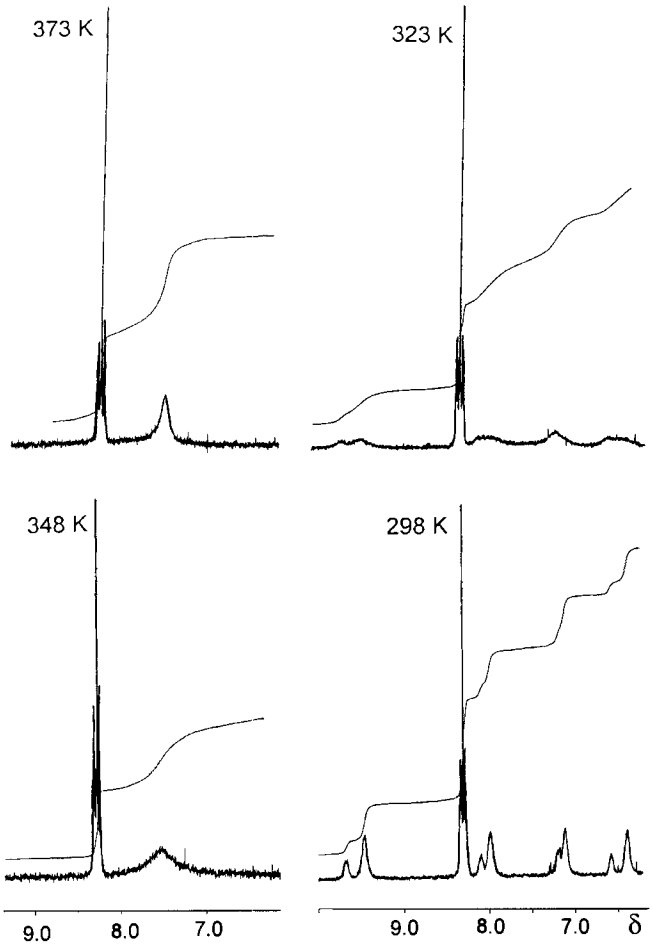

Figure 2. Temperature dependence of the ^{1}H-NMR spectra of Ce(PfOTTP)$_2$ ($C_2D_2Cl_4$, δ values, int. TMS, 300 MHz)

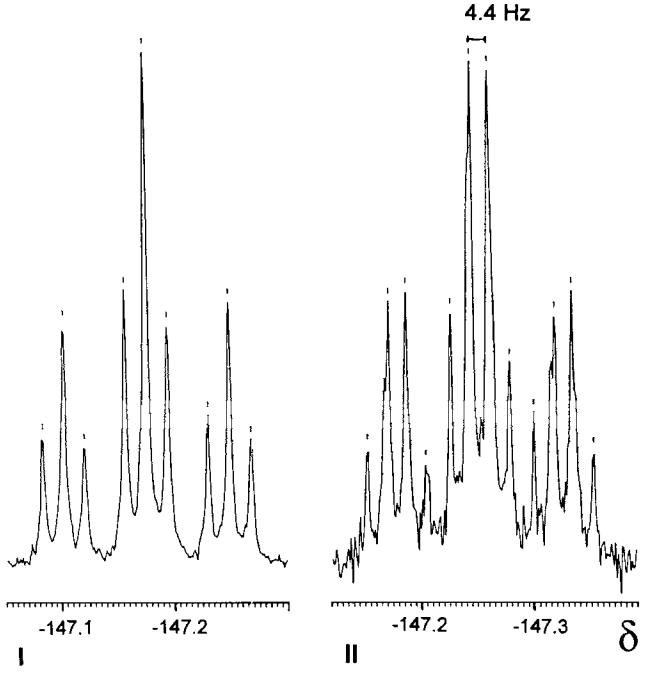

Figure 3. ^{19}F resonance signals of the *p*-F atoms of the free porphyrin **2f** (I) and the double-decker **1f** (II) ($CDCl_3$, δ scale, int. $CFCl_3$, 282 MHz, 303 K)

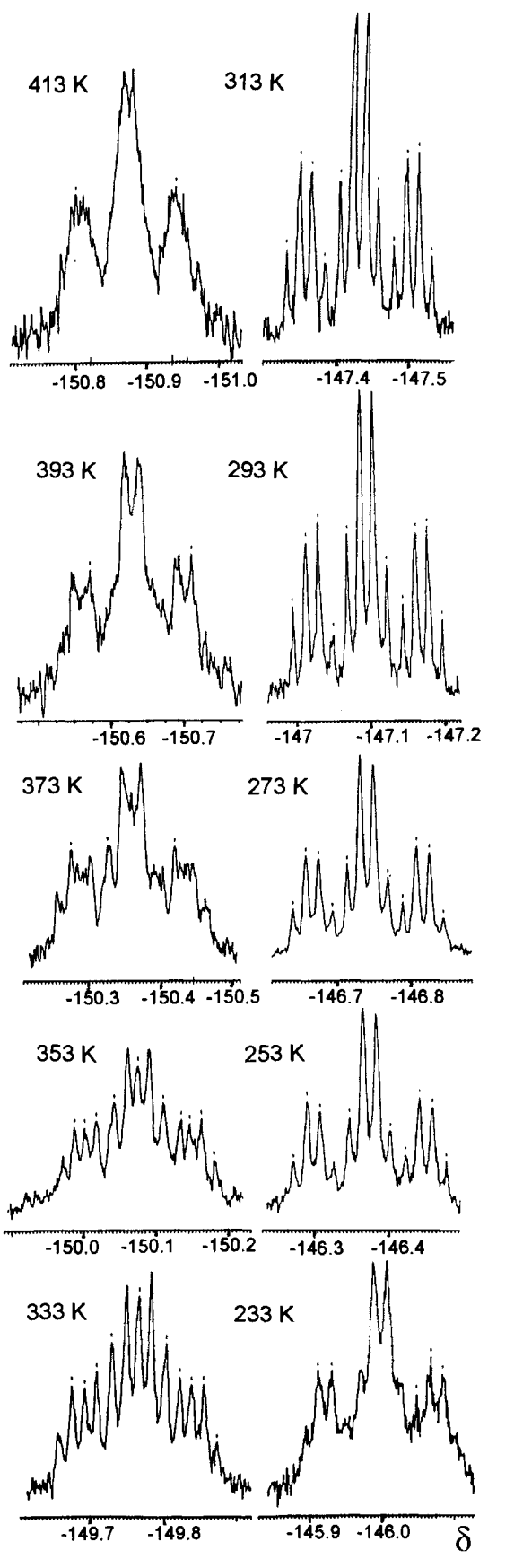

Figure 4. ^{19}F resonance signal of the *p*-F atom in Ce(PfOTTP)$_2$ (between 233 and 313 K, in $CDCl_3$, between 333 and 413 K in $C_2D_2Cl_4$, δ scale, int. $CFCl_3$, 282 MHz)

Experimental

MS: Varian MAT 311 A with data system SS 100 MS (direct insertion, ion source 150°C, field-ion desorption). – IR: Perkin Elmer 397, KBr pellets. – UV/Vis: Hewlett Packard HP 8451 A and Bruins Omega 10. – ^{1}H NMR: Bruker WM 300 (300 MHz), Bruker AM 500 (500 MHz). – ^{19}F NMR: Bruker AMX 300 (282 MHz). – Elemental analyses: Mr. F. Roth, microanalytical laboratory of the Institut für Organische Chemie der Technischen Hochschule Darmstadt or Analytische Laboratorien Malissa & Reuter, 51766 Engelskirchen.

The following chemicals were purchased from the companies indicated in parentheses: [D_1]chloroform, [D_2]dichloromethane, [D_2]tetrachloroethane, *n*-butyllithium (1.6 mol/l in *n*-hexane), 4-hydroxybenzaldehyde, 4-methylbenzaldehyde, silica gel for thin-layer chromatography type 60 G (Merck); benzoyl chloride, *p*-toluoyl chloride, pentafluorobenzoyl chloride (Fluka); alumina type W 200 super I, silica gel type 63–200 60 (Woelm ICN Biomedicals). 1,2,4-trichlorobenzene (TCB) was a gift of Bayer AG, Leverkusen, and dried by passing it through an alumina column (basic, super I). *p*-(Hydroxyphenyl)tris(*p*-tolyl)porphyrin[4] and Ce(acac)$_3$ · H_2O[18] (from $CeCl_3$, Johnson-Matthey) were prepared by literature methods. All solvents were distilled prior to use.

Protocol 1

5-(4-Methoxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, H_2(MeOTTP) (**2c**): To a solution of 170 mg (0.25 mmol) of H_2(HOTTP) and 200 mg (2.9 mmol) of NaOEt in 120 ml of toluene was added 2 ml (32 mmol) of methyl iodide. After stirring the solution at 40°C for 6 h, the solvent was evaporated in vacuo. The residue was chromatographed with chloroform on an alumina column (I, basic, 8 × 2.5 cm). Evaporation of the first red fraction yielded 136 mg (80%) of H_2(MeOTTP). – MS, *m/z* (%): 686 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419.6 nm (5.55), 517.1 (4.09), 553.2 (3.85), 592.5 (3.59), 648.0 (3.58). – IR (KBr), 5 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 1250 (OCH_3), 965, 735, 3320 (NH). – ^{1}H NMR ($CDCl_3$): δ = −2.76 (s, 2H, NH), 2.69 (s, 9H, tolyl CH_3), 4.08 (s, 3H, OCH_3), 7.27 (d, *J* = 8 Hz, 2H, oxyphenyl 3,5-H), 7.54 (d, *J* = 8 Hz, 6H, tolyl 3,5-H), 8.09 (d, *J* = 8 Hz, 6H, tolyl 2,6-H), 8.13 (m, 2H, oxyphenyl 2,6-H), 8.85 (m, 8H, pyrrole H).

Protocol 2: General procedure of the acylation of H_2(HOTTP) (**2b**) with benzoyl chloride, 4-methylbenzoyl chloride, and pentafluorobenzoyl chloride, respectively. – To a solution of 50 mg of H_2(HOTTP) in a mixture of 50 ml of chloroform and 5 ml of pyridine was added dropwise a solution of 1 ml of the appropriate acyl chloride in 5 ml of chloroform. After stirring for 2 h at 20°C, the solution was hydrolyzed with 50 ml of 0.1 N KOH and washed with water. The solvent was evaporated in vacuo and the residue chromatographed on an alumina column (II, neutral 7 × 2.5 cm) with chloroform. The first violet fraction contained the product. Evaporation of the solvent in vacuo and recrystallization from methanol yielded the following three (acyloxy)porphyrins **2d–f** as dark violet powders:

5-(4-Benzoyloxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin, H_2(BzOTTP) (**2d**): Yield 42 mg (73%). – MS, *m/z* (%): 776 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 418.7 nm (5.55), 516.2 (4.13), 551.7 (3.83), 591.0 (3.59), 646.9 (3.55). – IR (KBr), 7 most intense bands and NH vibration: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1200, 1260, 1170, 710, 1740 (C=O), 3320 (NH). – ^{1}H NMR ($CDCl_3$): δ = −2.77 (s, 2H, NH), 2.70 (s, 9H, tolyl CH_3), 7.59 (m, 8H, tolyl 3,5-H and benzoyl 3,5-H), 7.62 (d, *J* = 8 Hz, 2H, oxyphenyl 3,5-H), 7.71 (m, 1H, benzoyl 4-H), 8.10 (d, *J* = 8 Hz, 6H, tolyl 2,6-H), 8.26 (d, *J* = 8 Hz, 2H, oxyphenyl 2,6-H), 8.39 (d, *J* = 8 Hz, 2H, benzoyl 2,6-H), 8.87 (m, 8H, pyrrole H).

5-[4-(4-Methylbenzoyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrin, H_2(TuOTTP) (**2e**): Yield 38 mg (65%). – MS, *m/z* (%): 790 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.60), 516.2 (4.17), 551.4 (3.88), 591 (3.64), 647.2 (3.59). – IR (KBr), 7 most intense bands and NH vibration: $\tilde{\nu}$ = 1200 cm^{-1}, 800, 1170, 1180, 1270, 1740 (C=O), 1070, 3320 (NH). – ^{1}H NMR ($CDCl_3$): δ = −2.77 (s, 2H, NH), 2.51 (s, 3H, toluoyl CH_3), 2.71 (s, 9H, tolyl CH_3), 7.41 (d, *J* = 8 Hz, 2H, toluoyl 3,5-H), 7.56 (d, *J* = 8 Hz, 6H, tolyl 3,5-H), 7.62 (d, *J* = 8 Hz, 2H, oxyphenyl 3,5-H), 8.10 (d, *J* = 8 Hz, 6H, tolyl 2,6-H), 8.26 (d, *J* = 8 Hz, 2H, toluoyl 2,6-H), 8.28 (d, *J* = 8 Hz, 2H, oxyphenyl 2,6-H), 8.87 (m, 8H, pyrrole H).

10,15,20-Tris(4-methylphenyl)-5-[4-(2,3,4,5,6-pentafluorobenzoyloxy)phenyl]porphyrin, H_2(PfOTTP) (**2f**): Yield 29 mg (45%). – MS, *m/z* (%): 866 (100) [M^+]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 418.3 nm (5.62), 515.5 (4.19), 551.1 (3.88), 590.9 (3.65), 646.2 (3.60). – IR (KBr), 7 most intense bands and NH vibration: $\tilde{\nu}$ = 1210 cm^{-1}, 800, 1500, 1330, 970, 1755 (C=O), 740, 3320 (NH). – ^{1}H NMR ($CDCl_3$): δ = −2.78 (s, 2H, NH), 2.71 (s, 9H, tolyl CH_3), 7.56 (d, *J* = 8 Hz, 6H, tolyl 3,5-H), 7.65 (d, *J* = 8 Hz, 2H, oxyphenyl 3,5-H), 8.10 (d, *J* = 8 Hz, 6H, tolyl 2,6-H), 8.28 (d, *J* = 8 Hz, 2H, oxyphenyl 2,6-H), 8.86 (m, 8H, pyrrole H). – ^{19}F-NMR ($CDCl_3$): δ = −136.97 (m, 2 F, 2,6-F), −147.18 (tt, 1F, 4-F), −160.05 (m, 2F, 3,5-F).

Protocol 3

Bis[5-(4-hydroxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrinato]cerium(IV), Ce(HOTTP)$_2$ (**1b**): 2.4 mmol of *n*BuLi in 1.5 ml of hexane was added to a solution of 336 mg (0.5 mmol) of H_2(HOTTP) in 60 ml of TCB under a stream of nitrogen. The solution was stirred for 10 min at room temp. After adding 1.14 g of Ce(acac)$_3$ · H_2O (2.5 mmol), the solution was heated to reflux for 4 h. After cooling and removal of the TCB in vacuo the residue was treated with 15 ml of $CHCl_3$ and filtered.The filtrate was chromatographed on an alumina column (III, neutral, 3.5 × 10 cm). The first reddish-brown fraction was eluted with $CHCl_3$ and contained unreacted H_2(HOTTP). A second brown fraction was eluted with $CHCl_3$/MeOH (95:5) and contained the double decker Ce(HOTTP)$_2$. After evaporation of the solvent and recrystallization from chloroform/toluene (1:1) 220 mg (60%) of the product was obtained as a blue-violet powder. – MS, *m/z* (%): 810 (16) [^{140}Ce(HOTTP)$^+$], 672 (100) [H_2(HOTTP)$^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398.1 nm (5.36), 489.5 (4.18), 542.7 (4.03), 630.8 (3.57). – IR (KBr), 6 most intense bands and OH vibration: $\tilde{\nu}$ = 1660 cm^{-1}, 1640, 800, 980, 1440, 1230, 3350–3550 (OH). – $C_{94}H_{68}CeN_8O_2$ · 5 H_2O (1571.8): calcd. C 71.83, H 5.00, N 7.13; found C 71.18, H 5.13, N 7.13.

Protocol 4

Bis[5-(4-methoxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrinato]cer(IV), Ce(MeOTTP)$_2$ (**1c**): After the addition of 1.6 mmol of *n*BuLi in 1 ml of *n*-hexane and then 400 mg (0.88 mmol) of Ce(acac)$_3$ · H_2O to a solution of 120 mg (0.17 mmol) of H_2(MeOTTP) in 60 ml of TCB, the mixture was heated to reflux for 5 h. After filtration and evaporation of the solvent in vacuo, the residue was chromatographed on an alumina column (I, neutral, 8 × 2.5 cm). The first violet fraction [H_2(MeOTTP)] was eluted with toluene, the second brown fraction with chloroform. The latter yielded 48 mg (36%) of Ce(MeOTTP)$_2$ after evaporation of the solvent. – MS, *m/z* (%): 754 (23) [M^{2+}], 686 (100) [H_2(MeOTTP)$^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 398.1 nm (5.43), 487.0 (4.27), 543.2 (4.12), 630.3 (3.57). – IR (KBr), 6 most intense bands: $\tilde{\nu}$ = 795 cm^{-1}, 980, 1240 (OCH_3), 1170, 1320, 1510. – $C_{96}H_{72}CeN_8O_2$

(1509.8): calcd. C 76.37, H 4.81, N 7.42; found C 76.10, H 4.88, N 7.34.

Protocol 5: General procedure of the acylation of $Ce(HOTTP)_2$ (**1b**) with benzoyl chloride, 4-methylbenzoyl chloride, and pentafluorobenzoyl chloride, respectively. – A solution of 1 ml of the acyl chloride in 5 ml of chloroform was added dropwise to a solution of 100 mg (67 μmol) of $Ce(HOTTP)_2$ in 20 ml of chloroform and 10 ml of pyridine. After stirring for 2 h, the solution was poured into 50 ml of 0.1 N KOH. The organic layer was washed with 20 ml of water, dried, and the solvent distilled off in vacuo. Column chromatography (alumina, II, neutral, 7 × 2.5 cm) with $CHCl_3$ as eluent yielded a brown fraction containing the double-decker followed by a violet fraction containing the free porphyrin. In the case of **1f** preparative thin layer chromatography (silica gel plates, 20 × 20 cm, 1.25 mm) with toluene/dichloromethane (95:5) yielded the double-decker as the first fraction followed by a violet fraction containing the free porphyrin. Evaporation of the solvent and recrystallization from toluene/methanol (1:4) yielded the following double-deckers **1d**–**f** as brown-violet powders.

Bis{5-[4-(benzoyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrinato}cerium(IV), $Ce(BzOTTP)_2$ (**1d**): Yield 38 mg (33%). – MS, *m/z* (%): 844 (8) [M^{2+}], 776 [$H_2(BzOTTP)^+$] (100). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 397.2 nm (5.39), 489.5 (4.17), 542.6 (4.04), 631.1 (3.50). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1200, 1260, 1170, 710, 1740 (C=O). – $C_{108}H_{76}CeN_8O_4$ (1690.0): calcd. C 76.76, H 4.53, N 6.63; found C 76.80, H 4.69, N 6.73.

Bis{5-[4-(methylbenzoyloxy)phenyl]-10,15,20-tris(4-methylphenyl)porphyrinato}cerium(IV), $Ce(TuOTTP)_2$ (**1e**): Yield 43 mg (37%). – MS, *m/z* (%): 858 (25) [M^{2+}], 790 (100) [$H_2(TuOTTP)^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 397.7 nm (5.41), 487.5 (4.19), 542.5 (4.06), 630.1 (3.51). – IR (KBr), 7 most intense bands: $\tilde{\nu}$ = 800 cm^{-1}, 980, 1200, 1170, 1180, 1270, 1740 (C=O). – $C_{110}H_{80}CeN_8O_4$ (1718.0): calcd. C 76.90, H 4.69, N 6.52; found C 76.71, H 4.83, N 6.47.

Bis{10,15,20-tris(4-methylphenyl)-5-[4-(pentafluorobenzoyloxy)phenyl]porphyrinato}cerium(IV), $Ce(PfOTTP)_2$ (**1f**): Yield 24 mg (16%). – MS, *m/z* (%): 934 (86) [M^{2+}], (100) 934 [$H_2(PfOTTP)^+$]. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 397.7 nm (5.30), 488.0 (4.09), 542.5 (3.97), 630.1 (3.45). – IR (KBr), 6 most intense bands: $\tilde{\nu}$ = 1230 cm^{-1}, 1490, 985, 800, 1325, 1740 (C=O). – ^{19}F NMR ($CDCl_3$): δ = –136.95 (m, 2F, 2,6-F), –147.25 (m, 1F, 4-F), –160.03 (m, 2F, 3,5-F). – $C_{108}H_{66}CeF_{10}N_8O_4$ (1869.9): calcd. C 69.37, H 3.56, N 5.99; found C 69.20, H 3.80, N 5.74.

[1] Part LXV: J. W. Buchler, M. Eberle, P. Hammerschmitt, J. Hüttermann, R. Kappl, *Chem. Ber.* **1993**, *127*, 2619–2623.

[2] J. W. Buchler, V. Eiermann, H. Hanssum, G. Heinz, H. Rüterjans, M. Schwarzkopf, poster presented at the workshop for Magnetic Spectroscopy on Bioinorganic Transition Metal Centers, 24–27 February, **1993**, Homburg/Saar.

[3] Abbreviations used: $(P)^{2-}$, $(TPP)^{2-}$, $(TTP)^{2-}$: dianions of a general porphyrin, 5,10,15,20-tetraphenylporphyrin, and 5,10,15,20-tetrakis(4-methylphenyl)porphyrin, respectively; H(acac) = acetylacetone; TCB = 1,2,4-trichlorobenzene; pyr-H = pyrrole H atoms of the porphyrin ligand.

[4] J. W. Buchler, H. G. Kapellmann, M. Knoff, K. L. Lay, S. Pfeifer, *Z. Naturforsch., Teil B,* **1983**, *38*, 1339–1345.

[5] [5a] G. S. Girolami, S. N. Milam, K. N. Suslick, *Inorg. Chem.* **1987**, *26*, 343–344. – [5b] G. S. Girolami, S. N. Milam, K. N. Suslick, *J. Am. Chem. Soc.* **1988**, *110*, 2011–2012.

[6] [6a] J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, R. Weiss, *Chem. Ber.* **1991**, *124*, 1051–1058. – [6b] J. W. Buchler, A. De Cian, S. Elschner, J. Fischer, P. Hammerschmitt, R. Weiss, *Chem. Ber.* **1992**, *125*, 107–115.

[7] S.-H. Cho, G. S. Girolami, P. A. Gorlin, H.-J. Kim, K. Kim, W. S. Lee, K. S. Suslick, *Inorg. Chem.* **1991**, *30*, 2652–2656.

[8] [8a] J. W. Buchler, K. Elsässer, M. Kihn-Botulinski, B. Scharbert, *Angew. Chem.* **1986**, *98*, 257–258; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 286–287. – [8b] J. W. Buchler, *Comments Inorg. Chem.* **1987**, *6*, 175–191. – [8c] J. W. Buchler, B. Scharbert, *J. Am. Chem. Soc.* **1988**, *110*, 4272–4276.

[9] [9a] J. Deisenhofer, O. Epp, R. Huber, H. Michel, K. Miki, *J. Mol. Biol.* **1984**, *180*, 385–398. – [9b] J. Deisenhofer, O. Epp, R. Huber, H. Michel, K. Miki, *Nature* **1985**, *318*, 618–624. – [9c] J. Deisenhofer, R. Huber, H. Michel, *Nachr. Chem. Tech. Lab.* **1986**, *34*, 416–422.

[10] J. W. Buchler, M. Kihn-Botulinski, J. Löffler, B. Scharbert, *New. J. Chem.* **1992**, *16*, 545–553, and references cited therein.

[11] J. A. Anton, J. A. Ibers, R. G. Little, P. A. Loach, *J. Heterocycl. Chem.* **1975**, *12*, 343–349.

[12] J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, J. Löffler, B. Scharbert, R. Weiss, *Chem. Ber.* **1989**, *122*, 2219–2228.

[13] P. Hammerschmitt, Ph. D. Thesis, Technische Hochschule, Darmstadt, **1990**.

[14] G. Heinz, Diplomarbeit, Technische Hochschule Darmstadt, **1990**.

[15] [15a] E. F. Mooney, *An Introduction to ^{19}F-NMR Spectroscopy*, Heyden/Sadtler, London, **1970**. – [15b] K. J. Karel, F. J. Weigert, *J. Fluorine Chem.* **1987**, *37*, 125–149.

[16] [16a] G. R. Eaton, S. S. Eaton, *J. Chem. Soc., Chem. Commun.* **1974**, 576. – [16b] G. R. Eaton, S. S. Eaton, *J. Am. Chem. Soc.* **1977**, *99*, 6594.

[17] G. S. Girolami, P. A. Gorlin, K. S. Suslick, *Abstracts of Papers*, 205th ACS National Meeting, Denver, CO, American Chemical Society, Washington, DC, **1993**, Abstract 504.

[18] C. N. Mc Carty, L. L. Quill, J. G. Stites, *J. Am. Chem. Soc.* **1948**, *70*, 3142–3143.

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