"Geländer" Helical Molecules[**]

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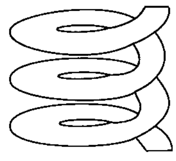
Asymmetric catalysis[1] with biphenyl and binaphthyl compounds as chiral ligands results in high enantiomeric excesses.[2] We here report on extended atropisomeric compounds which can serve as a basis for the development of new chiral inductors.

The doubly bridged *p*-terphenylophanes **2**–**4** offer a long type of screw-shaped molecule which had hitherto not been accessible: In contrast to helicenes, whose form is reminiscent of the shape taken by the steps of a spiral staircase (**I**),[3] *ortho*-bridged terphenyls resemble the banisters (German: "Geländer") of such a staircase, which are vertical to the steps (**II**). Owing to the elongated screw shape, **2**–**4** are expected to reveal high chirality like the helicenes.[4] The question arises whether the elongation of the screw (from biphenylo- to terphenylophanes) leads to an increased optical rotation as with the helicenes[3] and doubly helical oligoesters.[5] Clamping the terphenyls with suitable bridging elements should lead to stable conformers at room temperature. Substitution at the position *meta* to the bridges raises their stability on account of sterical hinderance.[6] Racemization barriers and the influence of substituents and bridges on these compounds have been well examined for biphenyls.[7] The solubility of the new helicenes has been increased with *tert*-butyl groups (**4**) and ester-containing bridges (**2b**, **3b**). The synthesis of **2**–**4** is described in Schemes 1 and 2; the fourfold functionalization with *N*-bromosuccinimide (NBS) is the key step.



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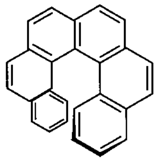

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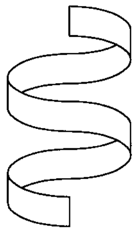

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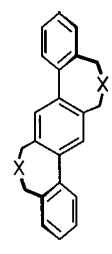

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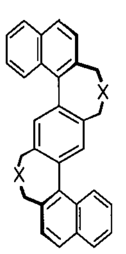

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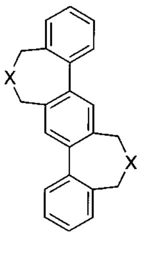
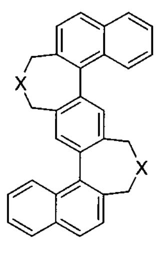
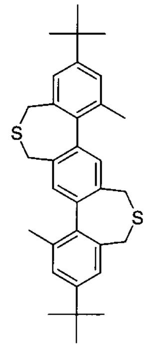


2a: X = S
2b: X = C(CO_2Et)$_2$



3a: X = S
3b: X = C(CO_2Et)$_2$



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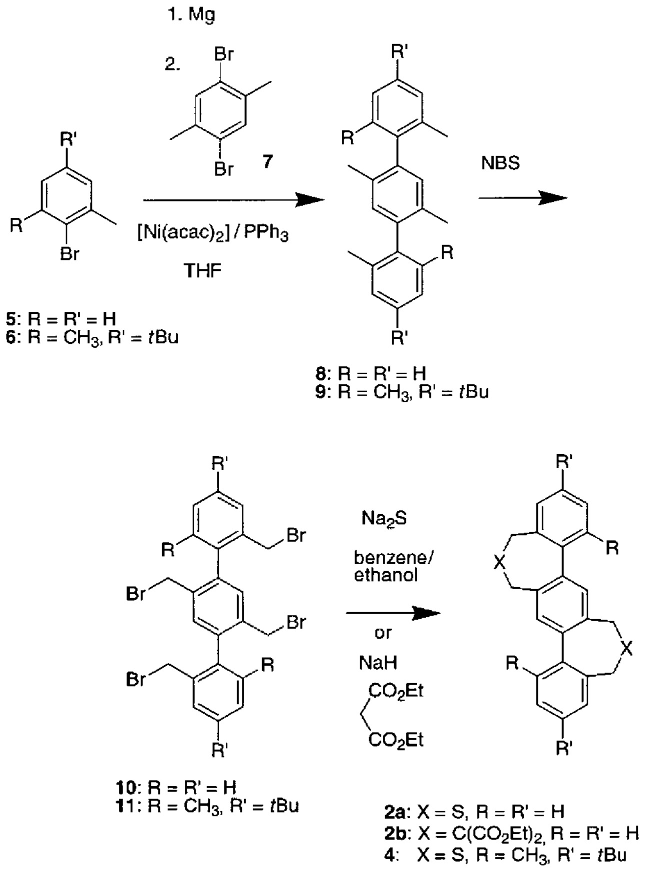

Scheme 1. Synthesis of **2a**, **2b**, and **4**.

We provided the helical terphenylophane **4** with *tert*-butyl groups to improve the solubility and with methyl groups to raise the racemization barrier. For these geländer helices three stable conformations are possible (Scheme 3). Owing to the hindered rotation about the biphenyl axis and the resulting fixation of the bridges in **2**–**4**, the ^{1}H NMR spectra show geminal couplings of the methyl protons and thus AB systems. There and in the ^{13}C NMR spectra separate signals are observed for the *meso* as well as for the chiral conformers.

The intended sterical hindrance of the methyl groups in **4** or of the naphthalene units in **3a** and **4b** causes an increase in the racemization/inversion barrier relative to those of helices **2a** and **2b**. High-temperature ^{1}H NMR experiments in DMSO

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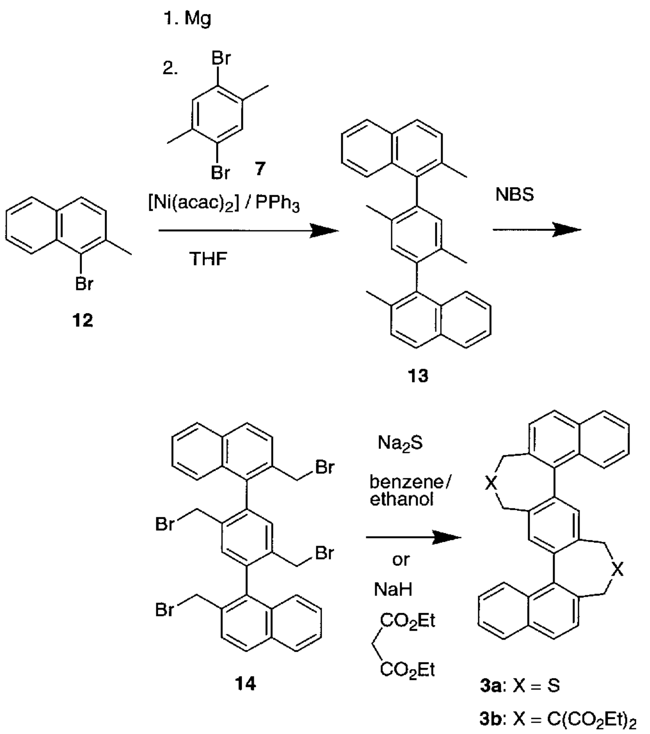
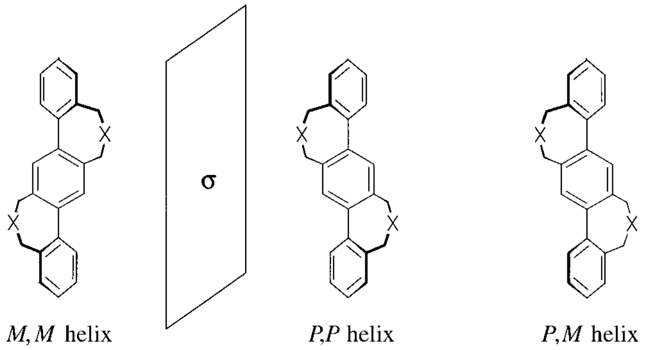


Scheme 2. Synthesis of **3a** and **3b**.



Scheme 3. Twisted terphenylophanes form three different conformers: two chiral und one *meso* form with an inversion center.

provided $\Delta G^{\neq} > 95\,\mathrm{kJ\,mol^{-1}}$ for **3a** and **3b**. The influence of the sulfur atoms in **2a**, **3a**, and **4** and of the ester substituents in **2b** and **3b** on bond lengths and angles is reflected in the conformational flexibility of the aliphatic bridge. The ester groups increase the energy barrier for the arene–arene rotation in comparison to an unsubstituted propano bridge; this is known for the corresponding biphenyls.[8]

The helices **3a** and **3b** could be separated into their conformers on a chiral HPLC column (cellulose tris(3,5-dimethylphenylcarbamate) (CDMPC),[9] eluent *n*-hexane/2-propanol (200/1), flow rate $1.5\,\mathrm{mL\,min^{-1}}$, $T = 0\,^{\circ}\mathrm{C}$); **3b** could only be enantiomerically enriched. The circular dichroism (CD) spectrum of the enantiomers of **3a** (Figure 1) shows intensive negative and positive Cotton effects. At 233 nm they are very intensive ($\Delta\varepsilon = +274$, $-265\,\mathrm{L\,mol^{-1}cm^{-1}}$; $g = 3.5\times10^{-2}$), the other three maxima ($\lambda = 251$ nm, $\Delta\varepsilon = \pm7\,\mathrm{L\,mol^{-1}cm^{-1}}$, $g = 3.5\times10^{-3}$; $\lambda = 265$ nm, $\Delta\varepsilon = \pm34\,\mathrm{L\,mol^{-1}cm^{-1}}$, $g = 2\times10^{-2}$; $\lambda = 308$ nm, $\Delta\varepsilon = 41$, $-43\,\mathrm{L\,mol^{-1}cm^{-1}}$, $g = 2.8\times10^{-2}$) have $\Delta\varepsilon$ values of less than ±50. The specific rotation of the geländer helix **3a** is also quite large ($[\alpha]^{20}_{365} = +2608$, -2612 in CH_2Cl_2). Thus, this new helix type even surpasses some helicenes known for high rotatory strength (and molar rotation) or inherently chiral fullerenes[10] with regard to the $\Delta\varepsilon$ values.

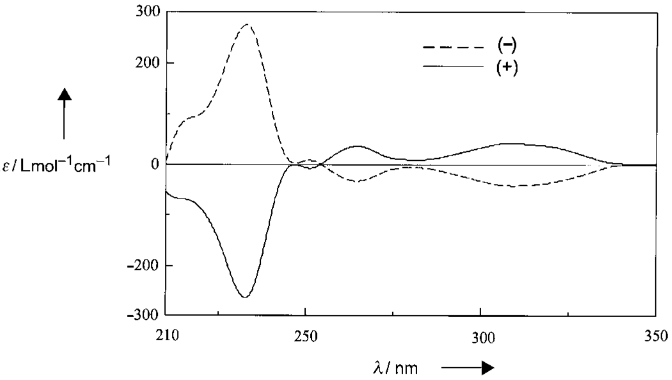


Figure 1. CD spectrum of **3a** (in CH_2Cl_2); CD spectrometer J-720, Jasco, Tokyo.

Colorless crystals of **3b** obtained from DMSO contained only the *meso* form, as the X-ray structure analyses showed (Figure 2a). The separation of the stereoisomers on the chiral HPLC column (see above) proved the *meso* conformer to be formed in excess relative to the enantiomeric forms. A single crystal of **3a** isolated from *n*-hexane/chloroform contained all three possible conformers *MM*, *PM*, and *PP* (Figure 2b).

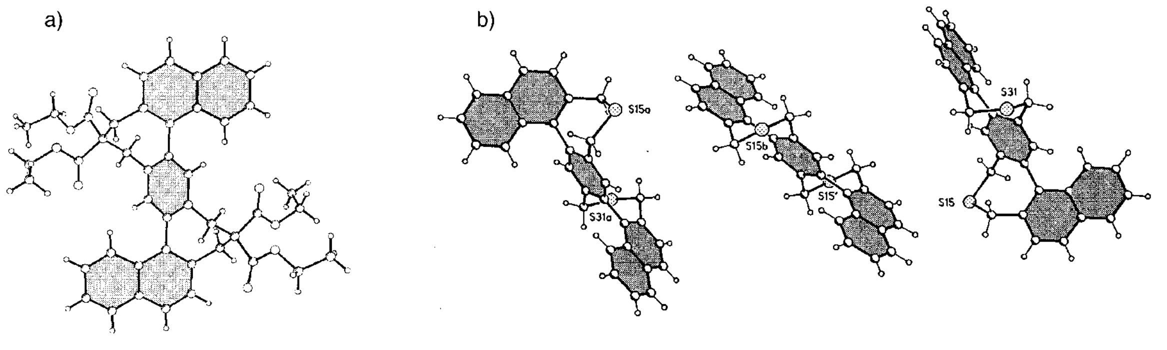


Figure 2. a) Crystal structure of (*P,M*)-**3b**; torsion angles 2-1-1′-2′: −48.0(3)°; **3b** has C_i symmetry, and the angle between the two naphthyl rings is 180°. b) Crystal structure of **3a**, which contains all three conformers; the chiral forms have C_2 symmetry, and the angle between the two naphthyl rings is 73°. The *meso* conformer has the same symmetry as **3b**. Torsion angles for the achiral molecule in the middle: 2-1-1′-2′: 54.9(2)°; torsion angles for the chiral molecules: 2-1-1′-2′: −52.6(2)°; 3′,4′,1″,2″: −53.3(2)°.

Remarkably, some of the crystals reveal optical activity. Solutions of these crystals gave distinct CD spectra, although the *n*-hexane/chloroform mother liquor was not optically active. Separation by HPLC under the conditions described above showed that the crystals contained different fractions of the stereoisomers.[11] A crystal whose solution shows a (+) rotation consists of approximately 20 % of the *meso* form, 60 % of the (+) enantiomer, and 20 % of the (−) enantiomer (a different crystal with (−) rotation in solution is made up of 20 % of the *meso* form, 30 % of the (+) enantiomer, and 50 % of the (−) enantiomer).

The CD spectrum of (*M*,*M*)-**3a** could be theoretically deduced.[12] Figure 3 shows the calculated spectrum, which is very similar to the experimental one (Figure 1) and which allows the determination of the absolute configuration.

As predicted, the elongation of biphenylo- to terphenylophanes results in high rotation values and distinct circular dichroisms. Thus, the geländer helices belong to the group of compounds with the highest $\Delta\varepsilon$ values. We now plan to investigate to what extent these compounds are suitable as ligands[13] in asymmetric catalysis.

Experimental Section

3a: Compound **14** (400 mg, 0.57 mmol) dissolved in benzene (200 mL) was slowly added through a precision dropping funnel to a suspension of sodium sulfide plates (60 %; 410 mg, 3.15 mmol) in ethanol/benzene (500 mL, 1/1 v/v); the addition required 7 h. After the mixture was heated at reflux for another 12 h, the solvent was removed in vacuo. Purification of the residue by column chromatography on silica gel (elution with petroleum ether (40/60)/CH_2Cl_2, 3/1; $R_f = 0.18$) gave 139 mg (55 % yield) of a colorless solid; m.p. 332 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.3-3.8$ (m, 8H), 7.4–7.6 (m, 8H), 7.9–8.1 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 31.70$, 31.80, 32.64, 32.68 (all CH_2S), 125.97, 126.05, 126.77, 126.83, 126.87, 127.10, 128.77, 128.81, 129.44, 129.48, 130.95, 131.03, 131.52, 133.06, 133.75, 133.78, 135.58, 135.85, 135.90, 138.39; MS (EI): *m/z* (%): 446.2 (100) [M^+ ($C_{30}H_{22}S_2$)], 367.2 (37), 353 (13); $[\alpha]^{20}_{365} = +2608, -2612$, $[\alpha]^{20}_{436} = +301, -308$ in CH_2Cl_2.

3b: Under an argon atmosphere sodium hydride (60 %; 137 mg, 3.4 mmol) was washed with *n*-hexane by decanting. Then toluene (30 mL) and diethyl malonate (274 mg, 1.7 mmol) were added, and the mixture was heated under reflux for 2 h. Compound **14** (300 mg, 0.43 mmol) dissolved in toluene (20 mL) was added dropwise to the boiling suspension. After the mixture was heated for another 10 h, the solvent was removed in vacuo. The residue was purified by column chromatography on silca gel (elution with CH_2Cl_2/petroleum ether (40/60), 3/1; $R_f = 0.52$) to yield 70 mg (24 %) of a colorless solid; m.p. 248 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.02$ (t, ^3J(H,H) = 7.1 Hz, 6H, CH_3), 1.10 (t, ^3J(H,H) = 7.1 Hz, 6H, CH_3), 3.35, 3.48 (d, ^2J(H,H) = 13.8 Hz, 4H, CH_2), 3.58, 3.76 (d, ^2J(H,H) = 13.8 Hz, 4H, CH_2), 3.99–4.16 (m, 4H, OCH_2), 4.23–4.35 (m, 4H, OCH_2), 7.43–7.49 (m, 2H), 7.65–7.72 (m, 4H), 7.74 (s, 2H), 7.78 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.84 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.72 (d, ^3J(H,H) = 8.4 Hz, 2H); ^{13}C NMR (250 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 14.35$, 14.26 (all CH_3), 30.45 (C), 36.85, 37.67 (all CH_2), 61.71, 65.28 (all OCH_2), 125.46, 126.19, 126.41, 127.88, 128.27, 128.35, 131.32, 132.34, 133.24, 133.70, 134.90, 135.94, 136.94, 170.89 (CO_2); MS (FAB): *m/z* (%): 698.3 (100) [M^+ ($C_{44}H_{42}O_8$)], 625.3 (33) [$M^+ - C_3H_5O_2$]; elemental analysis calcd for $C_{44}H_{42}O_8 \cdot 0.13\,CH_2Cl_2$: C 74.68, H 6.00; found: C 74.67, H 6.21.

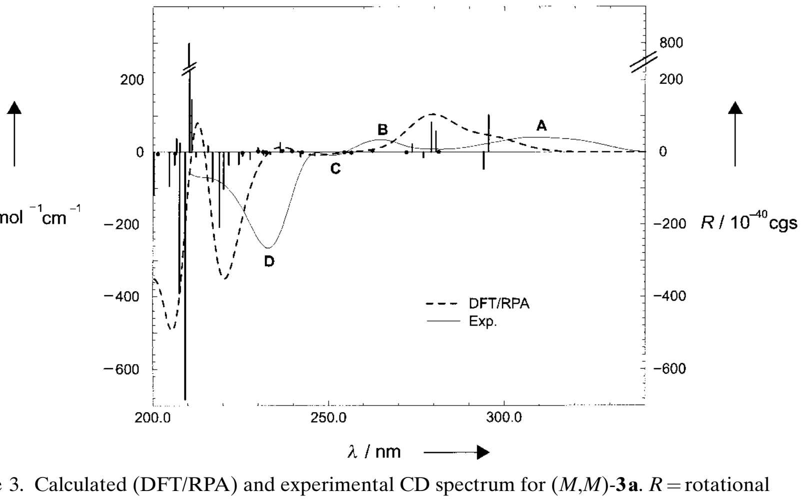


Figure 3. Calculated (DFT/RPA) and experimental CD spectrum for (*M*,*M*)-**3a**. R = rotational strength.

Crystal structure analyses: Single crystals of **3a** were obtained by slow evaporation of a solution of chloroform/hexane (1/1 v/v). Colorless single crystals of **3b** were obtained by cooling in DMSO. **3a** [**3b**] $C_{30}H_{22}S_2$ [$C_{44}H_{42}O_8$], Nonius Kappa-CCD [Nonius MACH 3], $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) [$Cu_{K\alpha}$ radiation ($\lambda = 154.178$ pm)], 123(2) [200] K, triclinic, $P\bar{1}$ (no. 2) [monoclinic, $P2_1/c$ (no. 14)]; $a = 1084.38(2)$ [1294.9(1)], $b = 1135.63(4)$ [1151.6(1)], $c = 1472.72(5)$ [1222.8(1)] pm, $\alpha = 73.222(2)°$, $\beta = 78.281(2)°$ [92.61(1)°], $\gamma = 74.078(2)°$, $V = 1.65458(9)$ [1.8216(3)] nm^3, $Z = 3$ [4], $\rho = 1.345$ [1.274] g cm^{-3}, crystal dimensions: 0.50 × 0.48 × 0.18 [0.43 × 0.40 × 0.20] mm, range for data collection $2\theta_{max} = 56°$ [140°], refections collected 26002 [3971], independent reflections 6171 [3418] ($R_{int} = 0.024$ [0.029]). The structures were solved by direct methods; non-hydrogen atoms were refined anisotropically on F^2, and hydrogen atoms with a riding model. The final R value $wR2$ (F^2) was 1.072 [1.036] for 433 [235] parameters. $R1 = 0.0323$ [0.067] (for $I > 2\sigma(I)$), $wR2 = 0.0907$ [0.1883] (all data). For **3b** an absorption correction on the basis of Ψ scans was applied. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101385. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] Theoretical methods: The geometry was optimized in C_2 symmetry with the TURBOMOLE[12a] suite of programs at the Hartree–Fock–SCF level. A split-valence (SV) basis set[12b] was used, which was augmented with a polarization d function ($\alpha_d = 0.55$) at the sulfur atoms. The CD spectrum (exitation energies and rotatory strength) was caculated with a method[12c,d] combining the Kohn–Sham density functional theory (DFT) and the random phase approximation (RPA).[12e] The DFT calculations were performed with the TURBOMOLE suite of programs, whereby the B3-LYP exchange-correlation functional[12f] and a SV(P) basis set ($\alpha_d(C) = 0.8$, $\alpha_d(S) = 0.55$) were employed. In this case (and in usual) this method—containing only global empirical parameters, which are not adjusted to specific molecular systems—leads to errors in the excitation energies below 0.3 eV. A portion of the deviations from the experimental spectrum can possibly be explained by solvent effects. a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; c) S. Grimme, *Chem. Phys. Lett.* **1996**, *259*, 128–137; d) S. Grimme, Habilitationsschrift, Universität Bonn, **1996**; e) T. H. Dunning, V. McKoy, *J. Chem. Phys.* **1967**, *47*, 1735–1747; f) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[13] We have already synthesized from **14** the tetrakis(diphenylphosphanyl oxide) compound, which can be reduced to tetraphosphane.

Modified, Amorphous Titania—A Hybrid Semiconductor for Detoxification and Current Generation by Visible Light**

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Although titania (titanium dioxide, TiO_2) absorbs only 2–3% of the solar light reaching the surface of the earth, it is the best investigated semiconductor in the field of chemical conversion and storage of solar energy. While early work was predominantly concerned with photoelectrochemical conversion,[1–3] later investigations focused on chemical processes, especially on water cleavage.[4] More recently, detoxification of water has become the main topic since upon UV irradiation in the presence of oxygen titania is able to oxidize most organic and inorganic contaminants to harmless products such as carbon dioxide and mineral acids.[5, 6]

According to the proposed mechanism, the light-generated electron-hole pair in titania is trapped at surface sites at which interfacial electron transfer occurs from and to adsorbed substrates.[7] To obtain a more efficient utilization of solar light ($\lambda_{max} = 500$ nm), diverse efforts were made to shift the light sensitivity of titania ($E_{bg} = 3.2$ eV, $\lambda \leq 390$ nm) into the visible region. A classical example is the photosensitization of the photocurrent by dyes and transition metal complexes of the type $[RuL_3]^{2+}$ (L = a substituted 2,2′-bipyridyl ligand).[8, 9] Doping with ions of V, Cr, Mn, Fe, Co, Ni, and Cu results in a shift of light absorption into the visible range, but only in very few cases does it also enable generation of a current or a chemical reaction by visible light.[10] An example is the decomposition of NO_x, although it is unclear whether or not this process occurs through a semiconductor photocatalysis mechanism.[11] It was further reported that colloidal titania doped with 0.1 to 50 atom% of iron induces the degradation of dichloroacetate with visible light. However, concomitant cathodic dissolution of the iron(III) oxide occurs, which can be avoided only by addition of oxidizing agents like hydrogen peroxide.[12]

Typical for all mentioned investigations is that the crystalline modifications anatase and rutile were involved, while amorphous titania was reported to not be photoactive.[13] In connection with our work on the use of amorphous zinc and cadmium sulfide as photocatalysts for new chemical syntheses,[14] we have now found that amorphous, microporous titania (AMM-Ti) modified with transition metal salts induces a photocurrent and photocatalyzes the degradation of 4-chlorophenol with visible light.

The new hybrid photocatalysts were prepared by a sol–gel procedure through controlled hydrolysis of titanium alkoxides in the presence of disodium hexachloroplatinate, rhodium(III) chloride, and gold(III) chloride[15]. The obtained microporous powders display specific surface areas in the range of 160–200 $m^2 g^{-1}$ and a pore-size distribution with a maximum at 0.78 nm, and are amorphous according to X-ray diffraction. In agreement with the latter, no crystalline parts could be detected by high-resolution transmission electron micrography. The ESCA and EXAFS investigations (ESCA = electron spectroscopy for chemical analysis, EXAFS = extended X-ray absorption fine structure) of a sample of AMM-Ti doped with 1.1% Pt^{IV} (**1**) revealed that platinum is present in the oxidation state IV and surrounded by four chloride ions. The EDX analyses (EDX = energy dispersive X-ray) with a lateral resolution of 1–2 nm do not give any evidence for the presence of discrete platinum particles. Therefore, it is assumed that platinum tetrachloride is homogeneously distributed in the matrix of amorphous titania.[16]

The diffuse reflectance spectrum of **1** resembles that of unmodified AMM-Ti, but exhibits an additional absorption in

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