An Easy Route for the Synthesis of New Axially Substituted Titanium(IV) Phthalocyanines

Markus Barthel,[a] Danilo Dini,[a] Sergej Vagin,[a] and Michael Hanack*[a]

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A facile synthesis of highly soluble, axially substituted titanium(IV) phthalocyanines is described. The reaction of tetra-*tert*-butylphthalocyaninatotitanium oxide tBu$_4$PcTiO with the chelating agents **3a**–**3i** containing oxygen or sulfur as donor atoms leads to the formation of axially substituted tBu$_4$PcTiX (X = functionalized catechols, dithiocatechol, and dihydroxynaphthalene). Following the same procedure a dimeric sandwich-like complex could be also synthesized from the reaction of tBu$_4$PcTiO with tetrahydroxy-*p*-benzoquinone. All compounds were characterized by IR, UV/Vis, MS, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. The axially substituted titanium phthalocyanines show high solubility and a low aggregation tendency due to the steric hindrance arising from the asymmetric peripheral substitution pattern of the macrocycle and the presence of bulky axial ligands. The relevant nonlinear optical (NLO) properties of some of the tBu$_4$PcTiX compounds were determined in order to evaluate the potential role of these new compounds in optical limiting. The correlation between tBu$_4$PcTiX structure and NLO properties is analyzed in terms of the electronic effects of the axial ligand.

Introduction

Phthalocyaninatotitanium(IV) oxide (PcTiO, **1**),[1] together with peripherally substituted R$_x$PcTiO and naphthalocyaninatotitanium(IV) oxides (R$_x$NcTiO) are an important class of compounds which has been thoroughly investigated for the photogeneration of charge carriers.[1–6] Previously we have shown that the presence of substituents at the periphery of phthalocyaninatotitanium oxides alters the electronic distribution of the ring as seen by the energy shift of some optical transitions,[7] and modifies drastically the molecular packing of the phthalocyanine in the solid state with relevant consequences for the electronic transport properties.[6,8,9] Another motive of interest in the preparation of PcTiO, R$_x$PcTiO, and related compounds relies upon the possibility of creating materials with remarkable nonlinear optical (NLO) properties.[10–15] In fact, PcTiO,[14] R$_x$PcTiO,[7] and analogous phthalocyanines[10,15] have some of the highest values of the third-order optical susceptibility $\chi^{(3)}$ among organic chromophores.[13,15] The reasons for this must be found in the presence of a large network of conjugated π-electrons, which confers high electrical polarizability to the Pc ring and offers the possibility of several kinds of electronic transitions in the UV/Vis spectral range.[16] Moreover, in PcTiO and related compounds the presence of the axial O ligand on the central Ti atom induces a perpendicular dipole moment with respect to the macrocycle plane, which alters the electronic structure of the macrocycle[17] and introduces new steric effects modifying the spatial relationships between neighboring molecules.[1] The presence of axial ligands can change the magnitude of the intermolecular interactions in the different axially substituted titanium(IV) phthalocyanines,[17] and is also expected to produce a favorable effect on the NLO properties of the resulting molecules, as previously verified with phthalocyanines possessing an analogous structure.[10,11,14,18,19] For these reasons we decided to develop an easy synthetic route for the preparation of new axially substituted titanium(IV) phthalocyanines, which is based upon the rupture of the Ti=O double bond in R$_x$PcTiO and the successive formation of two Ti–O or Ti–S single bonds.[17,20,21] The effect of the axial ligand change in R$_x$PcTiX compounds is also analyzed in terms of their NLO properties and optical limiting performance.[13]

Results and Discussions

Donor ligands like catechol or oxalic acid possess approximately the same reactivity towards PcTiO (**1**) and PcTiCl$_2$.[20] We have shown previously that axial ligand exchange reactions of **1** are possible with various chelating ligands.[17]

For the synthesis of the axially substituted titanium(IV) phthalocyanines, tBu$_4$PcTiO (**2**), as a mixture of structural isomers,[22,23] was heated with the chelating agents shown in Figure 1 [catechol (**3a**), dithiocatechol (**3b**), 2,3-naphthalenediol (**3c**), 4-*tert*-butylcatechol (**3d**), 3,4-dihydroxybenzaldehyde (**3e**), 2-(3,4-dihydroxyphenyl)acetonitrile[24]

[a] Institut für Organische Chemie, Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen, Germany
Fax: (internat.) +49-(0)7071/295-268
E-mail: hanack@uni-tuebingen.de

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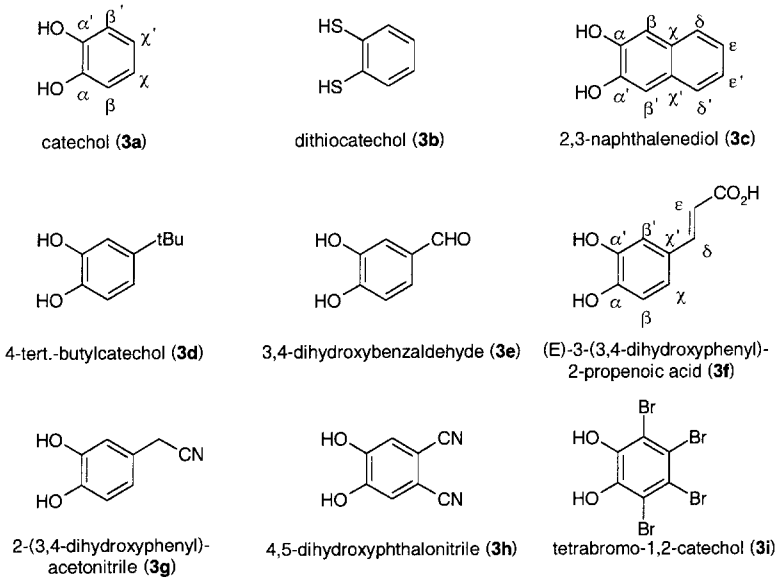
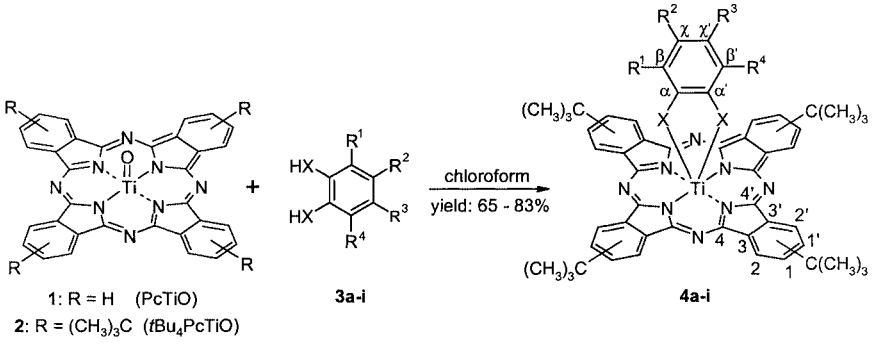


Figure 1. Various catechols and thiocatechol used as axial ligands and designation of their C and H atoms in the NMR spectra

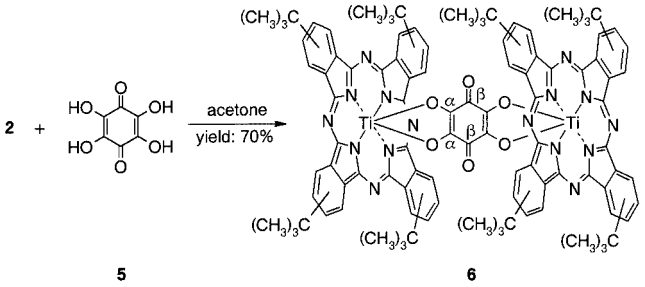


	X	R^1	R^2	R^3	R^4
3a, 4a	O	H	H	H	H
3b, 4b	S	H	H	H	H
3c, 4c	O	H	-(CH)$_4$-		H
3d, 4d	O	H	*t*Bu	H	H
3e, 4e	O	H	CHO	H	H
3f, 4f	O	H	-CH=CH-CO$_2$H	H	H
3g, 4g	O	H	CH_2CN	H	H
3h, 4h	O	H	CN	CN	H
3i, 4i	O	Br	Br	Br	Br

Scheme 1. Synthesis of axially substituted titanium(IV) phthalocyanines **4a**−**4i** and designation of their C and H atoms in NMR spectroscopic data

(**3g**), 4,5-dihydroxyphthalonitrile[25,26] (**3h**), (*E*)-3,4-dihydroxycinnamic acid (**3f**), tetrabromocatechol (**3i**)] in chloroform and successively purified by recrystallization from methanol/dichloromethane (1:1) (Scheme 1). The driving force of the reaction between **2** and **3a**−**3i** is based on the electrophilic character of titanium(IV) and the nucleophilic-

ity of oxygen and sulfur atoms in catechol- and thiocatechol-based derivatives.[27,28] The reaction of tetrahydroxy-*p*-benzoquinone (**5**)[29] leads to the dimeric complex (tBu$_4$PcTi)$_2$O$_4$(C$_6$O$_2$) (**6**) (Scheme 2). The large functionalized catechol ligands introduce steric hindrance above the macrocycle plane of the complexes **4a**−**4i**, and should inhibit molecular aggregation. The presence of electron-withdrawing substituents like CN, CHO, CH$_2$CN, and Br in the catechol-based ligands **3e**, **3g**, **3h**, **3i** induces additional electronic effects consisting of a large charge separation and the localization of a partial positive charge on the axial aromatic ring.



Scheme 2. Synthesis of the dimeric complex **6**

The 1,2-arrangement of the hydroxy or thio groups in the ligands **3a**−**3i** is essential for the reaction between **2** and **3a**−**3i**. The obtained complexes **4a**−**4i** contain five-membered organotitanium rings. These moieties possess a higher stability with respect to four-, six-, seven-, or eight-membered rings, and the formation of five-membered rings implies less angular strain between the oxygen-centered bonds of the moiety. Complexes of **2** with naphthalene-1,8-dicarboxylic acid, phthalic acid, squaric acid, 2,4-pentanediol, and maleic acid as axial ligands could not be formed under the same conditions as for the preparation of **4a**−**4i**. The axial substituents **3e**−**3g** containing the functional groups aldehyde, carboxylic acid and nitrile don't need to be protected during the reaction.

The reaction of **2** with the catechols and thiocatechol **3a**−**3i**, shown in Figure 1, gave the products **4a**−**4i**, which were purified by recrystallization as purification by column chromatography often leads to decomposition. Compounds **4a**−**4i** were obtained in high purity as verified by NMR spectroscopy. The axial ligand addition in **2** is fast and can take place even at room temperature by mixing the catechol with **2** in the solid state. The axially substituted complexes **4a**−**4i** are generally stable in the solid state, with the chelating agent allowing the saturation of the coordination in Ti^{IV}. The stability of solutions of **4a**−**4i**, for example in chloroform or dichloromethane, against sunlight depends on the nature of the axial substituent. Axially substituted titanium phthalocyanines with catechol-based ligands possessing electron donating groups, such as *tert*-butyl in **4d**, show a higher tendency to decompose than those phthalocyanines with electron-withdrawing cyano- (**4h**), bromo- (**4i**), or thio-substituted (**4b**) catechols as axial ligands. This is due to the different stability of the two single Ti−O bonds caused by the variation of the electron density as determined by the electronic nature of the substituents in the axial catechol. Generally the bonds between a transition metal and oxygen are more stable when the polarity of the bond is higher. The presence of electron-withdrawing groups on the catechol ligand increases the polar character of the Ti−O bond by polarizing the benzene moiety which connects electronically the electron-withdrawing group with the catechol oxygen atoms. Electron-donating groups on the axial catechol ligand should therefore induce a weakening of the Ti−O bond and give the opposite effect.

For the characterization of compounds **4a**−**4i** different NMR spectroscopic methods were applied. In the ^{1}H NMR spectra the phthalocyanine unit gives a characteristic resonance pattern in the aromatic region caused by the tetra substitution at the periphery, with two multiplets, one in the region between δ = 9 and 9.5 ppm for the eight protons in the 1,4-positions and one additional multiplet between δ = 8.3 and 9 ppm for the four protons in the 2,3-positions. The signal for the 36 protons of the *tert*-butyl substituents of the Pc ring usually appears at δ = 1.9 ppm as an intense and slightly broad signal due to the structural isomers, which give slightly split singlets. This general spectrum is valid for all compounds **4a**−**4i** and also for the dimeric complex **6**. The protons of the axial ligands, in general, give upfield-shifted signals due to the phthalocyanine ring-current effect.[30,31] These signals are found between δ = 3 and 6 ppm. By comparing the signal of the free ligands **3a**−**3i** and the signal of the same ligands coordinated by titanium(IV) in the axially substituted phthalocyanines **4a**−**4i**, we were able to confirm the structure of complexes **4a**−**4i** by integrating the different signals.

The ^{13}C NMR spectra of **4a**−**4i** can be analyzed by considering the signals produced by the peripheral substituents and the signals produced by the carbon atoms of the macrocycle separately. The peripheral substituents give two signals for the methyl groups and one signal of lower intensity for the quaternary carbon atom of the *t*Bu groups. These signals fall in the region δ = 30−35 ppm. The macrocycle carbon atoms give seven signals located between δ = 120 and 155 ppm. The carbon atoms linked to the nitrogen atoms are chemically quasi-equivalent and give a multiplet at δ = 151−152 ppm due to peripheral tetra-substitution, which leads to a mixture of structural isomers. The ^{13}C NMR signals of the axial ligands are distributed over the whole recorded range, going from the carbon of the aldehyde group of **4e** at δ = 190.5 ppm, to the aromatic carbon signals between δ = 100 and 120 ppm. The signals of the *tert*-butyl groups in **4d** are located between δ = 31 and 33 ppm. A distinction between the CH (or CH$_3$) signals and CH$_2$ (or quaternary carbon) signals in the complexes **4b**, **4f**, **4g**, and **4i**, could be achieved by DEPT experiments. The results confirmed the given assignments.

The UV/Vis maxima of the starting material tBu$_4$PcTiO (**2**), the axially substituted complexes **4a**−**4i** and the dimeric complex **6** (in CHCl$_3$) are listed in Table 1. The compounds **4b** (dithiocatechol substituted) and **4d** (4-*t*Bu catechol substituted) are characterized by a blue shift of both the Q- and B-band caused by the electron-donating ability of the

axial components with respect to *t*Bu$_4$PcTiO (**2**; Figure 2). On the other hand, compounds **4a**, **4c**, **4e**−**4i** show a red shift of the Q- and B-band which is caused by the electron-withdrawing aldehyde, carboxy, cyano and bromo substituents, respectively. The dimeric complex **6** has practically the same absorption bands as the monomer **2**, and has a greenish color both in the solid state and in solution. A comparison of the UV/Vis spectrum of **2** with those of compounds **4a**−**4i** shows an increase of the absorbance in the region of 500 nm for the species **4a**−**4i**, which is especially noticeable in the case of **4b**. This is caused by charge-transfer transitions between titanium(IV) and sulfur or oxygen. Moreover, a broadening of the Q- and B-bands can be observed. The broadening and splitting of the Q-band in some of the spectra of **4a**−**4i** (Figure 2) is caused by exciton interactions between the phthalocyanine and the axial ligand. The modification of the absorption pattern is generated by the coupling of two distinct transition dipole moments.[32−34] These effects are evident in the spectra of **4h** and **4i** — the complexes with the strongest electron-withdrawing substituents in the axial position (Figure 1). Exciton coupling can also cause additional absorption bands. In the case of large axial dipole moments the Q-bands of the resulting axially substituted phthalocyanines are mostly split and not broadened.

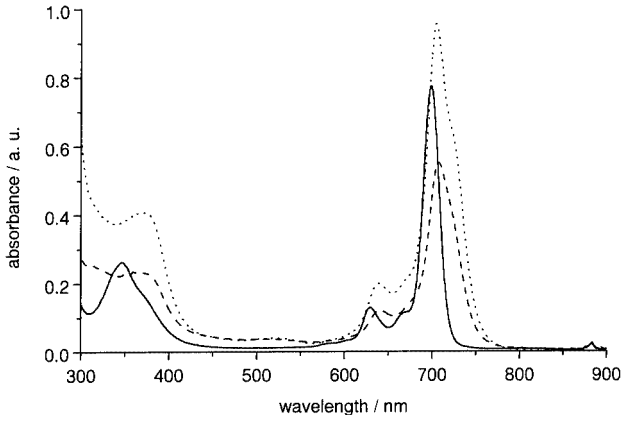


Figure 2. UV/Vis spectra of *t*Bu$_4$PcTiO (**2**, solid line), **4h** (cyano-substituted catechol derivative, dashed) and **4i** (bromo-substituted catechol derivative, dotted)

Table 1. Main UV/Vis absorption maxima of the phthalocyanines **2**, **4a**−**4i**, and **6** (solvent: chloroform)

	B [nm]	$Q_{1.0}$ [nm]	$Q_{0.0}$ [nm]	Shoulder [nm]
2	347.0	629.5	699.0	−
4a	347.5	633.0	702.0	−
4b	347.0	631.0	697.0	−
4c	352.5	634.0	703.0	−
4d	347.5	631.0	695.5	−
4e	354.0	635.0	702.0	−
4f	347.0	634.5	702.0	−
4g	348.5	633.0	701.5	−
4h	371.0	639.0	705.0	724.0
4i	359.5	639.5	707.5	726.0
6	346.0	630.5	699.5	−

The characteristic stretching vibration of Ti=O in the IR spectra of PcTiO (**1**)[25] and *t*Bu$_4$PcTiO (**2**) at $\tilde{\nu}$ = 972 cm^{-1} is absent in the IR spectra of **4a**−**4i** and **6**. This indicates the replacement of oxygen with the different chelating ligands **3a**−**3i** at the central titanium atom in **2**. The characteristic bands of the ligand functional groups are found in the IR spectra at 1684 cm^{-1} (aldehyde function) for **4e**, at around 3000 cm^{-1} and 1717 cm^{-1} (carboxy group) for **4f**, and at 2226 cm^{-1} (cyano group) for **4h**.

Phthalocyanines are one of the most important classes of materials for advanced applications based on nonlinear optical properties.[13,15,35] These include electro-optic modulators,[36] optical switching,[37] and optical limiters[13,35] among others.[36] In particular, optical limiters based on the mechanism of excited-state absorption of phthalocyanines give the most convincing outcomes.[10,13,15] The reasons for this are found in the combination of various favorable features in the structure of phthalocyanines, which produces molecular systems with strong optical limiting.[13,15,38] The optical-limiting effect is based on the variation of the material transmittance as a function of the incident light intensity. For practical purposes high transmittance (> 70%) at low incident light intensities (< 200 W·cm^{-2}), and strongly reduced transmittance under high intensity irradiation are desirable.[39] Some of the compounds reported here were studied with the *Z*-scan technique[40] in order to evaluate the possible role of the axial modification upon the nonlinear transmission properties. A comparison of the nonlinear transmission of compounds **2**, **4d**, **4h**, and **6** is given in Figure 3; the transmittance of the phthalocyanine solutions at low levels of irradiation ranges in the interval 90−95% (linear transmission at fluence < 1 J·cm^{-2}). In terms of optical limiting performance, the data in Figure 3 show that axial ligand change in *t*Bu$_4$PcTiO (**2**) is advantageous when the axial ligand possesses electron-withdrawing groups[11] such as CN (compound **4h**). The presence of electron-donating groups, such as *t*Bu, in the axial ligand does not bring about

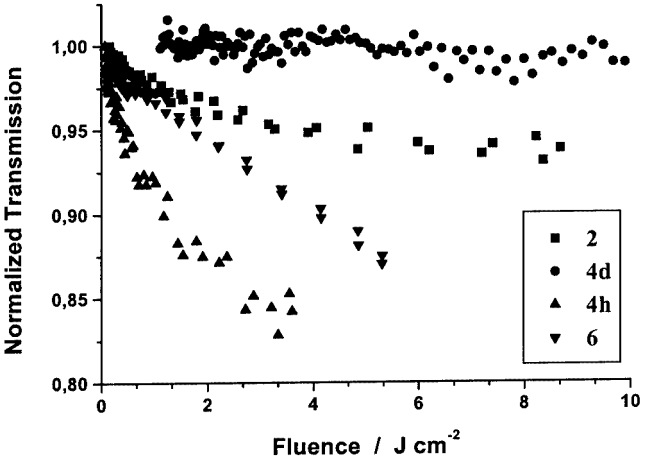


Figure 3. Nonlinear transmission curves of *t*Bu$_4$PcTiO (**2**), *t*Bu$_4$PcTi[O$_2$(C$_6$H$_3$)*t*Bu] (**4d**), *t*Bu$_4$PcTi[O$_2$(C$_6$H$_2$)(CN)$_2$] (**4h**), and (*t*Bu$_4$PcTi)$_2$[O$_2$(C$_6$O$_2$)O$_2$] (**6**) solutions in toluene at 532 nm; samples concentrations: 1 × 10^{-5} M; range of linear transmittance for the solutions: 90−95%; sample thickness: 0.1 cm; light intensity at the focus: 8 × 10^8 W·cm^{-2}

any improvement in the resulting limiting effect of **4d** as proved by the almost unchanged transmission of the material in the whole range of applied light fluences. Dimerization of titanium(IV) phthalocyanines through the bridging species tetrahydroxy-*p*-benzoquinone produces a system (**6**) which shows an intermediate performance between **2** and **4h**. Due to the symmetrical structure of the dimer **6**, the improvement of the nonlinear optical behavior of **6** with respect to **2** is not due to an increase of the axial dipole moment as in **4h**, but probably due to the higher number of active absorbing moieties per molecular unit.

Conclusions

An easy procedure for the change of axial ligands in titanium(IV) phthalocyanines has been presented. *t*Bu_4PcTiO (**2**) can be treated with several catechol- and thiocatechol-based derivatives to afford the axially substituted titanium(IV)phthalocyanines **4a**−**4i**. The ligand exchange reaction of titanium(IV)phthalocyanine does not require special conditions. The new catechol-substituted species were fully characterized spectroscopically. The nonlinear transmission of some derivatives has been measured and a non-trivial correlation between the nonlinear transmission of the axially substituted titanium(IV) phthalocyanines and the electronic nature of the substituents on the axial ligand has been found.

Experimental Section

General: All reactions were carried out without exclusion of air. 4-*tert*-Butylphthalonitrile,[22,23] 3,4-(dihydroxyphenyl)acetonitrile[24] (**3g**), 4,5-dihydroxyphthalonitrile[25,26] (**3h**), and tetrahydroxy-*p*-benzoquinone[29] (**5**) were prepared according to literature procedures. The starting material *t*Bu_4PcTiO (**2**) has been mentioned in the patent literature, but without any further details on preparation. We modified a reported strategy[41] and describe the synthesis here also.

FT-IR: Bruker IFS 48. UV/Vis: Shimadzu UV-365. MS: Varian Mat 711 (FD, temperature of the ion source: 30 °C); Finnigan TSQ 70 MAT (EI, temperature of the ion source: 200 °C, electron energy 70 eV). ^{1}H, ^{13}C NMR, DEPT^{135}: Bruker AC 250 (^{1}H: 250.131 MHz, ^{13}C: 62.902 MHz). Elemental Analyses: Carlo−Erba Elemental Analyser 1104, 1106. Due to the known difficulties in the combustion of phthalocyanines and naphthalocyanines, it was not possible to obtain satisfactory elemental analysis data for all described compounds.

2,(3)-(Tetra-*tert*-butylphthalocyaninato)titanium(IV) Oxide (2): 4-*tert*-Butylphthalonitrile[22,23] (1.0 g, 5.44 mmol), urea (180 mg, 3 mmol) and three drops of DBU (1,8-Diazabicyclo[5.4.0]undec-7-en) were mixed in 15 mL of 1-pentanol and heated to 120 °C. At that temperature Ti(OBu)$_4$ (0.51 mL, 1.5 mmol) was added with a syringe, and the reaction mixture was refluxed for 7 h at 155 °C. After cooling to room temperature the mixture was poured into 400 mL of methanol and precipitation was induced by adding approximately 50 mL of water dropwise. The crude product was collected by centrifugation and dried in vacuo. The obtained mixture of metalated and metal-free phthalocyanine was purified by column chromatography on silica gel. Elution with a mixture of toluene/chloroform (1:1) gave the metal-free *t*Bu_4PcH_2. The main product *t*Bu_4PcTiO (**2**) was obtained by changing the eluent to pure chloroform. Pure **2** was obtained by recrystallization from dichloromethane by addition of methanol. Yield: 380 mg (35%), m.p. > 300 °C; blue microcrystalline powder. ^{1}H NMR ($CDCl_3$): δ = 1.95−1.89 (s, 36 H, CH_3), 8.39−8.29 (m, 4 H, H-1), 9.23−9.12 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.10 [C(*C*H_3)$_3$], 36.25 [*C*(CH_3)$_3$], 120.1−119.7 (C-2′), 123.5−123.2 (C-2), 128.9−128.8 (C-1), 134.9−134.5 (C-3), 137.4−136.8 (C-3′), 151.9−150.9 (C-4,4′), 154.9−154.6 (C-1′) ppm. UV/Vis ($CHCl_3$): λ_{max} = 699.0 nm, 629.5, 347.0. IR (KBr): $\tilde{\nu}$ = 2956 s, 2905 s, 2363 m, 2338 m, 1734 w, 1718 s, 1616 w, 1489 s, 1394 w, 1364 w, 1325 w, 1256 w, 1072 m, 972 m, 829 w, 692 w cm^{-1}. $C_{48}H_{48}N_8OTi$ (800.84): calcd. C 71.99, H 6.04, N 13.99; found C 71.36, H 5.91, N 13.91. MS (FD): *m*/*z* = 801.0 [M$^+$].

General Procedure for the Preparation of Axially Substituted Phthalocyanines 4a−4i: *t*Bu_4PcTiO (**2**; 100 mg, 0.125 mmol) and 0.25 mmol of the appropriate catechol-based axial ligand were dissolved in 100 mL of $CHCl_3$ and heated for 1 h under reflux. After cooling to room temperature the solvent was removed in vacuo and the crude product was recrystallized from dichloromethane by addition of methanol. After collecting the precipitate and washing with methanol the product was dried under vacuum.

(Catecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV) (4a): Prepared from catechol (**3a**; 27.5 mg, 0.25 mmol); yield 78 mg (70%); green powder, m.p > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.98−1.79 (s, 36 H, CH_3), 4.38−4.17 (m, 2 H, H-χ,χ′), 5.46−5.27 (m, 2 H, H-β,β′), 8.42−8.32 (m, 4 H, H-1), 9.57−9.18 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.1 [C(*C*H_3)$_3$], 36.2 [*C*(CH_3)$_3$], 108.2 (C-χ,χ′), 119.3 [C-β,β′), 119.8−119.5 (C-2′), 123.3−123.1 (C-2), 128.9−128.8 (C-1), 134.3−133.9 (C-3), 136.7−136.2 (C-3′), 152.6−151.6 (C-4,4′), 154.9−154.6 (C-1′), 157.5 (C-α,α′) ppm. UV/Vis ($CHCl_3$): λ_{max} = 702.0 nm, 633.0, 347.5. IR (KBr): $\tilde{\nu}$ = 2957 vs, 2903 s, 2864 s, 1612 s, 1504 s, 1483 s, 1460 s, 1394 s, 1364 s, 1325 vs, 1281 s, 1254 vs, 1200 m, 1151 s, 1097 m, 1078 vs, 1024 w, 926 s, 914 w, 893 m, 860 w, 849 w, 829 s, 820 s, 756 vs, 694 m, 669 m, 646 m cm^{-1}. $C_{54}H_{52}N_8O_2Ti$ (892.94): calcd. C 72.64, H 5.87, N 12.55; found C 72.35, H 5.81, N 12.45. MS (FD): *m*/*z* = 892.5 [M$^+$].

(Dithiocatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) (4b): Prepared from dithiocatechol (**3b**; 36 mg, 0.25 mmol); yield: 82 mg (71%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.97−1.80 (s, 36 H, CH_3), 5.34−5.17 (m, 2 H, H-χ,χ′), 5.99−5.84 (m, 2 H, H-β,β′), 8.42−8.33 (m, 4 H, H-1), 9.58−9.12 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.0 [C(*C*H_3)$_3$], 36.3 [*C*(CH_3)$_3$], 120.0−119.5 (C-2′), 122.8 (C-χ,χ′), 123.6−123.2 (C-2), 124.9 (C-β,β′), 129.1 (C-1), 134.7−134.3 (C-3), 137.1−136.5 (C-3′), 149.4 (C-α,α′), 152.0−151.0 (C-4,4′), 155.0−154.7 (C-1′) ppm. DEPT^{135} ($CDCl_3$): δ = 32.5 [C(*C*H_3)$_3$], 120.4−120.0 (C-2′), 122.8 (C-χ,χ′), 123.8−123.6 (C-2), 125.3 (C-β,β′), 129.5 (C-1) ppm. UV/Vis ($CHCl_3$): λ_{max} = 697.0 nm, 631.0, 497.0, 347.0. IR (KBr): $\tilde{\nu}$ = 3146 m, 3063 m, 2957 vs, 2866 s, 2550 m, 2388 m, 1506 m, 1483 m, 1458 s, 1394 s, 1366 m, 1327 vs, 1281 m, 1256 vs, 1200 m, 1151 m, 1078 vs, 928 m, 829 m, 758 m cm^{-1}. $C_{54}H_{52}N_8S_2Ti$ (924.32): calcd. C 70.11, H 5.67, N 12.11, S 6.96; found C 69.49, H 5.72, N 11.78, S 6.91. MS (FD): *m*/*z* = 923.9 [M$^+$].

(2,3-Naphthalenediolato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) (4c): Prepared from 2,3-dihydroxynaphthalene (**3c**;

40 mg, 0.25 mmol); yield: 81 mg (70%); dark green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.91−1.83 (s, 36 H, CH_3), 4.63−4.49 (s, 2 H, H-β), 6.59−6.45 (m, 4 H, H-δ,δ′,ε,ε′), 8.42−8.32 (m, 4 H, H-1), 9.58−9.25 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.0 [C(CH_3)$_3$], 36.3 [C(CH$_3$)$_3$], 101.9−101.7 (C-α,α′), 120.0−119.5 (C-2′), 122.7−122.5 (C-β,β′), 123.5−123.1 (C-2), 126.7−126.5 (C-χ,χ′), 129.1−128.9 (C-1), 134.3−133.8 (C-3), 136.7−136.2 (C-3′), 152.7−151.5 (C-4,4′), 155.1−154.8 (C-1′), 158.4−158.3 (C-δ,δ′) ppm. UV/Vis ($CHCl_3$): λ_{max} = 703.0 nm, 634.0, 352.5. IR (KBr): $\tilde{\nu}$ = 2961 s, 2866 w, 1612 w, 1506 w, 1483 m, 1447 m, 1420 w, 1406 m, 1394 m, 1366 m, 1325 vs, 1281 m, 1256 vs, 1151 m, 1099 w, 1080 s, 1063 s, 928 m, 858 m, 829 m, 758 s, 694 w, 669 m, 640 s cm^{-1}. $C_{58}H_{54}N_8O_2Ti$ (942.38): calcd. C 73.87, H 5.77, N ; found C 72.10, H 5.08, N 11.09. MS (FD): *m*/*z* = 942.5 [M$^+$].

(4-*tert*-Butylcatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) (4d): Prepared from 4-*tert*-butylcatechol (**3d**; 42 mg, 0.25 mmol); yield: 93 mg (79%), green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 0.60−0.40 [s, 9 H, catechol-C(CH_3)$_3$], 1.99−1.73 [s, 36 H, C(CH_3)$_3$], 4.47−4.24 (m, 2 H, H-α′,χ), 5.71−5.57 (d, 1 H, H-β), 8.41−8.31 (m, 4 H, H-1), 9.58−9.26 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.8−30.4 [catechol-C(CH$_3$)$_3$], 31.1 [catechol-C(CH$_3$)$_3$], 32.5−31.8 [C(CH$_3$)$_3$], 36.2 [C(CH$_3$)$_3$], 108.4−107.9 (C-β′), 110.2−109.6 (C-β), 118.7−118.4 (C-χ), 119.9−119.4 (C-2′), 123.6−123.0 (C-2), 128.9−128.6 (C-1), 134.4 (C-3), 136.8−136.3 (C-3′), 152.6−151.5 (C-4,4′), 154.8−154.5 (C-1′) ppm. UV/Vis ($CHCl_3$): λ_{max} = 695.5 nm, 631.0, 347.5. IR (KBr): $\tilde{\nu}$ = 2957 vs, 2903 s, 2866 s, 1735 m, 1664 m, 1612 s, 1504 m, 1481 s, 1464 s, 1394 s, 1364 s, 1325 vs, 1281 s, 1256 vs, 1200 m, 1151 m, 1099 w, 1078 vs, 1024 w, 925 s, 893 m, 862 w, 829 s, 758 s, 694 m, 669 m, 644 w cm^{-1}. $C_{58}H_{60}N_8O_2Ti$ (949.05): calcd. C 73.40, H 6.37, N 11.81; found C 72.95, H 6.72, N 11.61. MS (FD): *m*/*z* = 948.7 [M$^+$].

(4-Formylcatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) (4e): Prepared from 3,4-dihydroxybenzaldehyde (**3e**; 34 mg, 0.25 mmol); yield: 88 mg (77%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.99−1.88 [m, 36 H, C(CH_3)$_3$], 4.39−4.18 (d, 1 H, H-β), 4.75−4.56 (d, 1 H, H-χ), 6.02−5.85 (s, 1 H, H-β′), 8.45−8.28 (m, 4 H, H-1), 8.78−8.66 (s, 1 H, CHO), 9.55−9.01 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.0 [C(CH$_3$)$_3$], 36.3 [C(CH$_3$)$_3$], 106.9 (C-β), 107.9 (C-β′), 120.1−119.3 (C-2′), 123.8−123.0 (C-2), 127.7 (C-χ′), 129.3−129.0 (C-1), 134.0−133.4 (C-3), 136.4−135.6 (C-3′), 152.4−151.0 (C-4,4′), 155.3−154.8 (C-1′), 158.1 (C-α′), 164.1 (C-α), 190.5 (CHO) ppm. UV/Vis ($CHCl_3$): λ_{max} = 702.0 nm, 635.0, 354.0. IR (KBr): $\tilde{\nu}$ = 2961 s, 2363 vs, 2338 s, 1734 s, 1717 s, 1699 m, 1695 s, 1684 vs, 1676 s, 1653 s, 1647 m, 1616 m, 1558 m, 1539 m, 1522 m, 1506 s, 1481 s, 1474 s, 1466 m, 1458 m, 1436 m, 1366 m, 1327 s, 1277 vs, 1256 s, 1065 s, 829 m, 756 m, 667 s, 656 m cm^{-1}. $C_{55}H_{52}N_8O_3Ti$ (920.36): calcd. C 71.73, H 5.69, N 12.17; found C 70.12, H 5.23, N 11.67. MS (FD): *m*/*z* = 920.1 [M$^+$].

{4-[(*E*)-2-Carboxyethenyl]-1,2-benzenediolato}-2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV) (4f): Prepared from (*E*)-3,4-dihydroxycinnamic acid (**3f**; 45 mg, 0.25 mmol); yield: 78 mg (65%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 2.24−1.60 [s, 36 H, C(CH_3)$_3$], 4.26−3.93 (d, 1 H, H-β), 4.53 (s, 1 H, H-β′), 5.10−4.91 (d, 1 H, H-ε), 5.50−5.30 (d, 1 H, H-χ), 6.55−6.40 (d, 1 H, H-δ), 8.42−8.21 (m, 4 H, H-1), 9.57−8.95 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.1 [C(CH$_3$)$_3$], 36.3 [C(CH$_3$)$_3$], 105.7 (C-β′), 107.6 (C-β), 112.3 (C-ε), 120.1−119.2 (C-2′), 121.8 (C-χ), 123.5−122.8 (C-2), 124.9 (C-χ′), 129.0 (C-1), 134.0−133.3 (C-3), 136.8−135.5 (C-3′), 146.8 (C-δ), 152.2−150.4 (C-4,4′), 155.0−154.2 (C-1′), 158.0 (C-α), 161.0 (C-α′), 171.7 (CO$_2$H) ppm. DEPT^{135} ($CDCl_3$): δ = 31.8 [C(CH$_3$)$_3$], 105.5 (C-β′), 107.3 (C-β), 112.0 (C-ε), 120.6−119.5 (C-2′), 121.5 (C-χ), 124.0−123.1 (C-2), 129.9−129.0 (C-1), 146.5 (C-δ) ppm. UV/Vis ($CHCl_3$): λ_{max} = 702.0 nm, 634.5, 347.0. IR (KBr): $\tilde{\nu}$ = 3159 m, 3064 m, 2958 s, 2904 s, 2866 s, 1778 m, 1717 s, 1684 s, 1616 s, 1568 s, 1504 vs, 1483 s, 1433 s, 1394 m, 1365 m, 1327 vs, 1256 vs, 1072 s, 831 m, 756 m, 671 s, 644 m cm^{-1}. $C_{57}H_{54}N_8O_4Ti$ (962.99): calcd. C 71.07, H 5.66, N 11.64; found C 69.25, H 5.33, N 11.28. MS (FD): *m*/*z* = 944.0 [M$^+$ − H_2O]; FAB: *m*/*z* = 962.3 [M$^+$].

(4-Cyanomethylcatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV) (4g): Prepared from 2-(3,4-dihydroxyphenyl)acetonitrile[24] (**3g**; 38 mg, 0.25 mmol); yield: 88 mg (76%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 2.07−1.79 [m, 36 H, C(CH_3)$_3$], 2.58−2.48 (s, 2 H, CH_2), 4.25−4.00 (m, 2 H, H-β,χ), 5.30−5.11 (s, 1 H, H-β′), 8.44−8.27 (m, 4 H, H-1), 9.56−9.03 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.9 (CH$_2$), 32.10 [C(CH$_3$)$_3$], 36.25 [C(CH$_3$)$_3$], 107.6−107.2 (C-β,β′), 117.6 (CN), 118.1−117.8 (C-χ), 120.0−119.3 (C-2′), 123.5−123.0 (C-2), 128.1−128.8 (C-1), 134.1−133.6 (C-3), 136.6−135.9 (C-3′), 152.3−151.9 (C-4,4′), 155.0−154.5 (C-1′), 157.4 (C-α), 158.2 (C-α′) ppm. DEPT^{135} ($CDCl_3$): δ = 22.3 (CH$_2$), 32.5 [C(CH$_3$)$_3$], 108.0−107.3 (C-β,β′), 118.5−118.2 (C-χ), 120.4−119.7 (C-2′), 123.9−123.3 (C-2), 129.7−129.2 (C-1) ppm. UV/Vis ($CHCl_3$): λ_{max} = 701.5 nm, 633.0, 348.5. IR (KBr): $\tilde{\nu}$ = 2959 vs, 2903 m, 2363 s, 2338 m, 1734 s, 1717 s, 1701 m, 1684 m, 1653 m, 1616 m, 156 s, 1474 s, 1466 m, 1458 m, 1394 m, 1364 m, 1325 vs, 1281 m, 1256 vs, 1148 m, 1063 vs, 1022 m, 926 m, 829 s, 808 m, 756 s, 692 m, 667 s, 652 s, 548 w cm^{-1}. $C_{56}H_{53}N_9O_2Ti$ (931.38): calcd. C 72.17, H 5.73, N 13.53; found C 71.20, H 5.58, N 13.31. MS (FD): *m*/*z* = 931.0 [M$^+$].

(4,5-Dicyanocatecholato)-2,(3)-(tetra-*tert*-butylphthalocyaninato)-titanium(IV) (4h): Prepared from 4,5-dihydroxyphthalonitrile[25,26] (**3h**; 40 mg, 0.25 mmol); yield: 77 mg (66%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 2.02−1.91 [m, 36 H, C(CH_3)$_3$], 4.52 (s, 2 H, H-β,β′), 8.50−8.29 (m, 4 H, H-1), 9.51−8.90 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.0 [C(CH$_3$)$_3$], 36.4 [C(CH$_3$)$_3$], 105.1 (C-χ,χ′), 111.9 (CN), 115.6 (C-β,β′), 120.1−119.3 (C-2′), 123.7−123.0 (C-2), 129.8−129.4 (C-1), 133.5−132.8 (C-3), 135.9−135.0 (C-3′), 152.1−150.9 (C-4,4′), 155.8−155.3 (C-1′), 160.5 (C-α,α′) ppm. UV/Vis ($CHCl_3$): λ_{max} = 724(sh) nm, 705.0, 639.0, 371.0. IR (KBr): $\tilde{\nu}$ = 2961 vs, 2905 w, 2868 w, 2363 m, 2338 m, 2226 m, 1734 m, 1717 s, 1701 m, 1684 w, 1653 w, 1612 w, 1539 w, 1522 m, 1506 m, 1487 vs, 1458 m, 1394 m, 1364 s, 1327 s, 1298 vs, 1256 s, 1067 s, 928 w, 860 m, 831 m, 756 m, 667 m, 598 s, 536 w cm^{-1}. $C_{56}H_{50}N_{10}O_2Ti$ (942.35): calcd. C 71.33, H 5.34, N 14.85; found C 70.88, H 4.74, N 13.66. MS (FD): *m*/*z* = 942.3 [M$^+$].

(Tetrabromocatecholato)-2,(3)-(tetra-tert-butylphthalocyaninato)-titanium(IV) (4i): Prepared from tetrabromocatechol (**3i**; 107 mg, 0.25 mmol); yield: 125 mg (83%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.99−1.86 [s, 36 H, C(CH$_3$)$_3$], 8.45−8.27 (m, 4 H, H-1), 9.55−8.97 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.1 [C(CH$_3$)$_3$], 36.3 [C(CH$_3$)$_3$], 103.0 (C-χ,χ′), 115.7 (C-β,β′), 120.1−119.2 (C-2′), 123.9−123.0 (C-2), 129.2 (C-1), 133.9−132.8 (C-3), 136.4−135.1 (C-3′), 152.5−150.7 (C-4,4′), 152.6 (C-α,α′), 155.5−154.9 (C-1′) ppm. DEPT^{135} ($CDCl_3$): δ = 32.5 [C(CH$_3$)$_3$], 120.5−119.7 (C-2′), 124.2−123.4 (C-2), 129.9−129.5 (C-1) ppm. UV/Vis ($CDCl_3$): λ_{max} = 726(sh) nm, 707.5, 639.5, 359.5. IR (KBr): $\tilde{\nu}$ = 3429 m, 2959 s, 2928 m, 2864 m, 2363 m, 2340 w, 1726 m, 1612 m, 1508 w, 1483 m, 1460 m, 1414 s, 1394 m, 1366 s, 1325 vs, 1281 m, 1256 vs, 1200 m, 1171 w, 1151 m, 1146 m, 1101 w, 1090 m, 1063 vs, 1045 m, 1028 m, 953 m, 926 m, 914 w, 893 w, 829

m, 752 s, 690 s, 667 s, 588 m, 530 w, 480 w, 418 w, 405 w cm^{-1}. $C_{54}H_{48}Br_4N_8O_2Ti$ (1208.52): calcd. C 53.67, H 4.00, N 9.27; found C 53.68, H 3.94, N 9.05. MS (FD): m/z = 1208.1 [M^+].

Bis[2,(3)-(tetra-*tert*-butylphthalocyaninato)titanium(IV)]-3,6-dioxo-1,4-cyclohexadiene-1,2,4,5-tetrolate (6): tBu$_4$PcTiO (**2**; 100 mg, 0.125 mmol) was dissolved in 200 mL of acetone and stirred intensively under reflux. Within 2 h, tetrahydroxy-*p*-benzoquinone[29] (**5**; 11 mg, 0.062 mmol) dissolved in 100 mL of acetone was added dropwise. The product precipitated due its lower solubility than the starting material. After cooling the crude product was collected by centrifugation and washed consecutively with toluene, ethyl acetate, and methanol. Drying in vacuo gave pure **6**. Yield: 76 mg (70%); green powder, m.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.97−1.67 [d, 36 H, $C(CH_3)_3$], 8.43−7.95 (m, 4 H, H-1), 9.51−8.69 (m, 8 H, H-2,2′) ppm. ^{13}C NMR ($CDCl_3$): δ = 32.3−31.7 [$C(CH_3)_3$], 36.3−36.0 [$C(CH_3)_3$], 120.2−119.0 (C-2′), 123.5−122.4 (C-2), 128.8 (C-1), 131.3 (C-α), 136.1−134.2 (C-3), 137.3−136.6 (C-3′), 152.3−150.4 (C-4,4′), 154.5 (C-1′), 164.2 (C-β) ppm. UV/Vis ($CDCl_3$): λ_{max} = 699.5 nm, 630.5, 346.0. IR (KBr): $\tilde{\nu}$ = 2959 vs, 2905 m, 2868 m, 1780 w, 1717 s, 1684 s, 1614 s, 1483 s, 1464 s, 1394 s, 1366 s, 1327 vs, 1281 s, 1256 vs, 1202 m, 1151 m, 1074 vs, 1026 w, 975 m, 928 s, 893 m, 849 w, 831 s, 760 s, 694 m, 671 m cm^{-1}. $C_{102}H_{96}N_{16}O_6Ti_2$ (1736.66): calcd. C 70.50, H 5.57, N 12.90; found C 69.74, H 5.34, N 12.28. MS (FD): m/z = 1736.4 [M^+].

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