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Titanium Phthalocyanines with Axial Phenylenevinylenes

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The synthesis of soluble titanium(IV) phthalocyanines, axially substituted with phenylenevinylenes (PVs) (R_xPcTiX), is described. The reaction of peripherally tetra- and octasubstituted (phthalocyaninato)titanium oxides (R_xPcTiO) **1**–**3** with chelating PV-diols **4a**–**4c** leads to the formation of axially substituted R_xPcTiX **5**–**7**. All compounds were characterized by IR, UV/Vis, MS, and ^{1}H NMR spectroscopy. Pcs **5**–**7** dissolved in dichloromethane are stable in the dark. The stability of solutions of **5**–**7** in sunlight depends on the nature of the peripheral substituents in the Pc ring and the chain length of the axial PV substituents.

Introduction

(Phthalocyaninato)titanium(IV) oxide (PcTiO) as well as their peripherally substituted derivatives (R_xPcTiO) and (naphthalocyaninato)titanium(IV) oxides (R_xNcTiO) have been extensively investigated for the photogeneration of charge carriers.[1–6] Substituted soluble R_xPcTiOs also show remarkable nonlinear optical (NLO) properties,[7–12] for example, they exhibit some of the highest values of third-order optical susceptibility χ^3 among organic chromophores.[10,12] This is due to the large network of conjugated π-electrons, which results in a high electrical polarizability of the Pc ring, and the perpendicular dipole moment with respect to the plane of the macrocycle that is induced by the axial O ligand on the Ti atom in all the PcTiO derivatives.[13] The presence of other axial ligands should have additional favorable effects on the NLO properties of such compounds. For this reason, highly soluble axially substituted titanium(IV) phthalocyanines have been synthesized in our group and their NLO properties (e.g., optical limiting properties) studied.[14] To prepare such compounds (tetra-*tert*-butylphthalocyaninato)titanium(IV) oxide [(tBu)$_4$-PcTiO] was treated with chelating agents, for example, catechols or dithiocatechol with oxygen or sulfur atoms as the donor atoms, to form axially substituted (tBu)$_4$PcTiX (X = functionalized catechols, dithiocatechol, 2,3-dihydroxynaphthalene). The correlation between the electronic effects of the various axial ligands in the (tBu)$_4$PcTiX structures and their NLO properties has been studied in detail.[14]

These investigations have now been extended to R_xPcTiX systems **5**–**7** in which phenylenevinylenes are connected to the central Ti atom in peripherally substituted Pcs (Scheme 1).

Pcs **5**–**7** containing phenylenevinylenes (PVs) as axial substituents with different chain lengths in comparison with those previously studied with axial catechol-substituted titanium phthalocyanines are expected to exhibit additional favorable NLO (optical limiting) properties.[14] Pcs **5**–**7** are even more important as so-called stopcock molecules in our ongoing investigations of host–guest compounds with photonic antenna systems in channels of perhydrotriphenylene (PHTP) or zeolite crystals loaded with axial fluorescent chains of **5**–**7**.[15] Stopcock molecules of this type can transport energy and/or electrons from its Pc head to its tail through the plugged channels of PHTP or zeolite.[15,16] To prepare the host–guest compounds the PcTiX systems must be completely soluble, for example, in dichloromethane, which is accomplished by the peripheral substituents in the Pc ring. In addition it was necessary to investigate whether or not Pcs of the type **5**–**7** are generally stable in solution. As we have shown previously,[14] axially substituted PcTi–catechol compounds are stable in chloroform or dichloromethane in the dark. The stability of the solutions in sunlight depends on the nature of the axial catechol. Electron-withdrawing groups on the catechol increase the polarity of the Ti–O bond in the PcTiX complexes, which leads to an increase in the Ti–O bond strength and thereby to a higher stability of the complexes.

Results and Discussion

The substituted (phthalocyaninato)titanium(IV) oxides **1**–**3** (Scheme 1), the starting materials for the preparation of compounds **5**–**7**, were obtained as follows. (Tetra-*tert*-butylphthalocyaninato)titanium(IV) oxide (**1**) (mixture of isomers) has been synthesized by us previously.[14] To prepare **2** (mixture of isomers), 4-[4-(1,1,3,3-tetramethylbutyl)-

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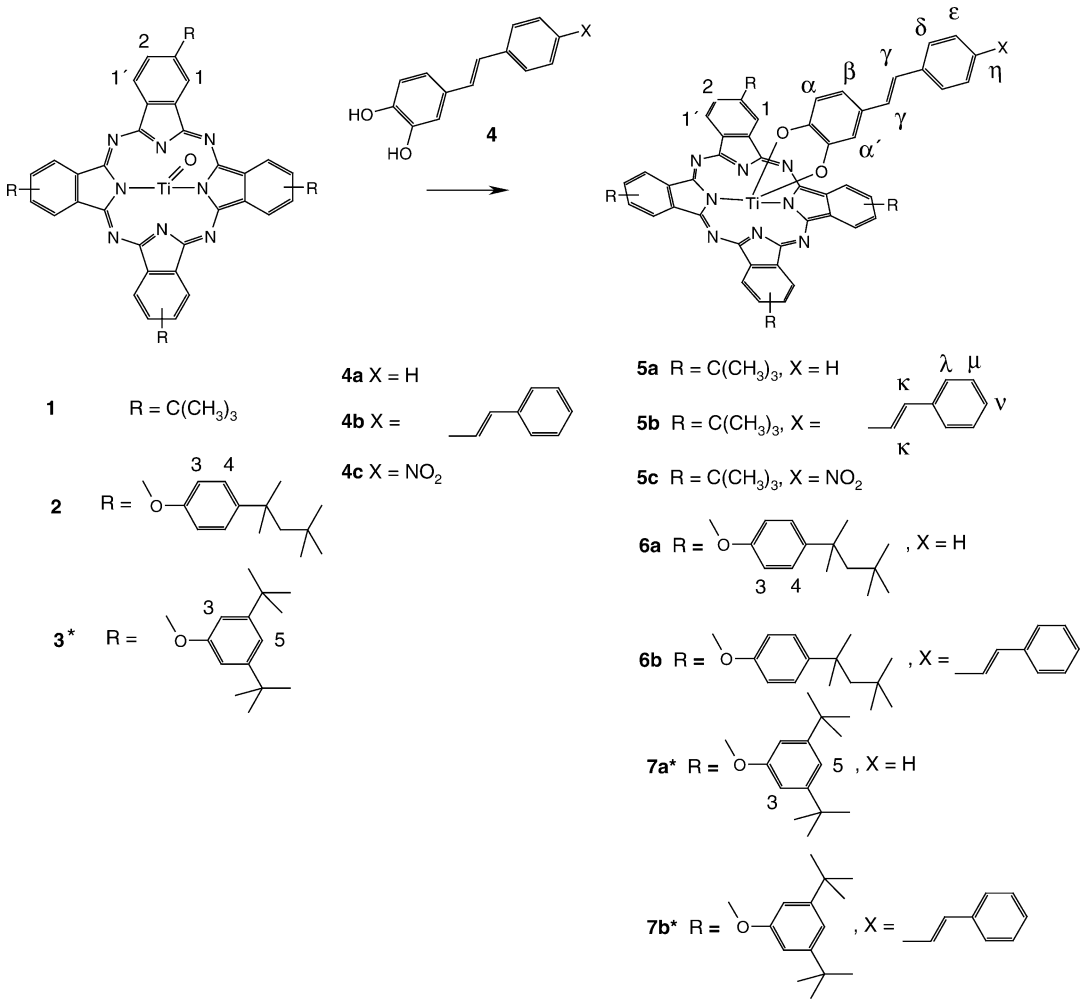


Scheme 1. Synthesis of axially PV-substituted titanium phthalocyanines **5**–**7**; * octasubsituted Pcs.

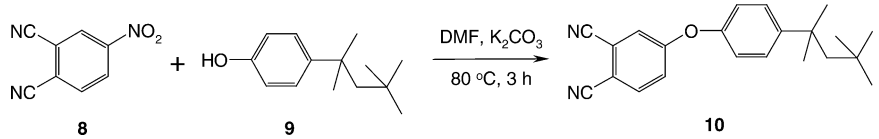
phenoxy]phthalonitrile (**10**) was treated with $Ti(OBu)_4$ in pentanol at 155 °C. Phthalonitrile **10** was obtained in good yield by nucleophilic substitution of the nitro group in 4-nitrophthalonitrile (**8**) with 4-(1,1,3,3-tetramethylbutyl)phenol (**9**) in DMF (Scheme 2).

The octasubstituted PcTiO **3** was obtained from 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile[17] using the same procedure as described for the synthesis of **2**. The UV/Vis spectrum of **3** shows a Q-band maximum at 705 nm (see Table 1).

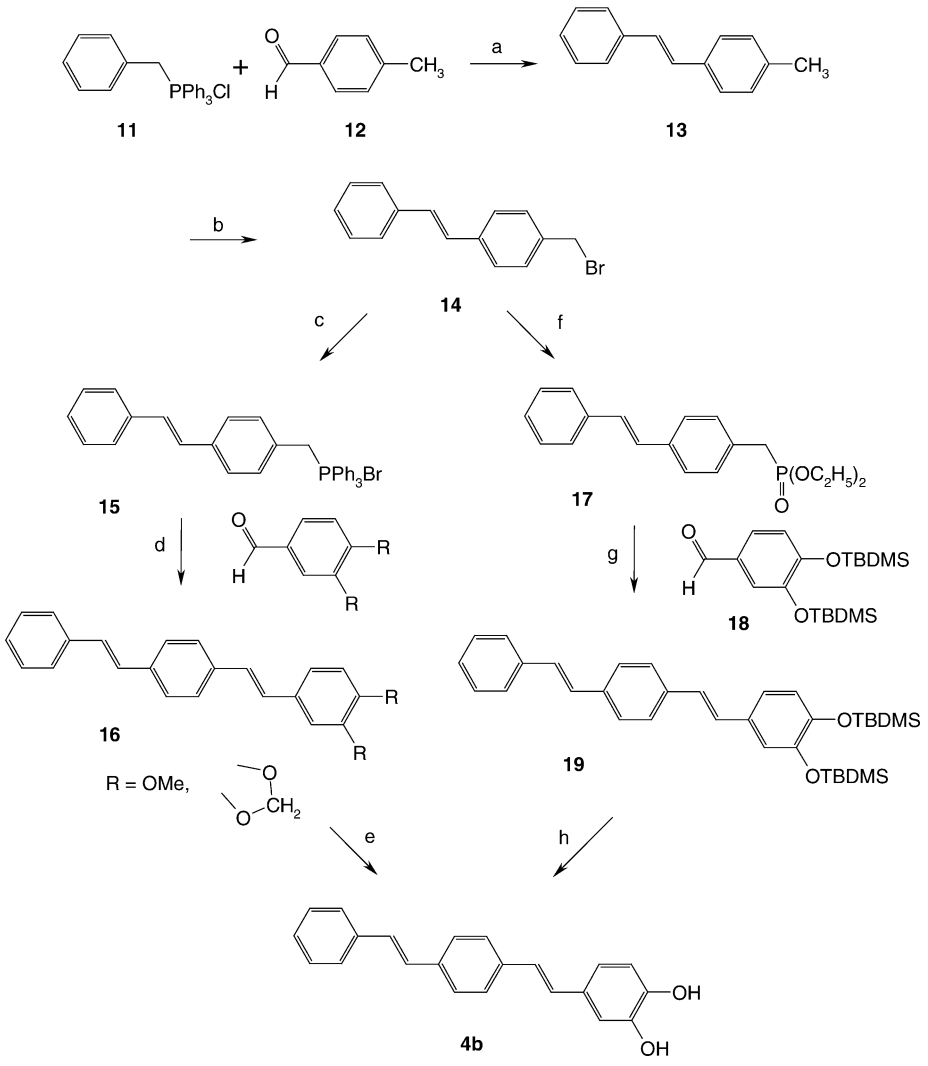
The axial ligand (*E*)-3,4-dihydroxy-4′-nitrostilbene (**4c**) was prepared by condensation of 4-nitrophenylacetic acid with 3,4-dihydroxybenzaldehyde.[18] (*E*)-3,4-Dihydroxystilbene (**4a**)[19] was prepared by Wittig reaction of benzyltriphenylphosphonium chloride (**11**)[20] with 3,4-dimethoxybenzaldehyde and subsequent ether cleavage with BBr_3.

In attempt to synthesize **4b**, (*E*)-4-methylstilbene (**13**)[21] was first transformed with NBS and AIBN into the benzyl bromide **14**[22] and subsequently into the phosphonium bromide **15** (Scheme 3).[23] The reaction of **15** with either 3,4-dimethoxybenzaldehyde or piperonal led to the ethers **16**[24] as a mixture of *E*/*Z* isomers. Compounds **16** were transformed into the pure *E* isomers by heating in THF with phenyl disulfide.[19] The intended ether cleavage of **16** with, for example, BBr_3 or AlI_3 in various solvents to obtain the target molecule **4b** was not successful.

Therefore a different route to the synthesis of **4b** was used (Scheme 3). Benzyl bromide **14** was transformed by an Arbuzov reaction[25] into diethyl (4-styrylbenzyl)phosphonate (**17**)[26] and further by a Horner–Emmons reaction[27] with bis(*tert*-butyldimethylsilyloxy)benzaldehyde (**18**)[28] into 1,2-bis(*tert*-butyldimethylsilyloxy)-4-[2-(4-styryl-



Scheme 2. Synthesis of 4-[4-(1,1,3,3-tetramethylbutyl)phenoxy]phthalonitrile (**10**).



Scheme 3. The preparation of 4-[2-(4-styrylphenyl)vinyl]benzene-1,2-diol (**4b**). Reagents and conditions: (a) *t*BuOK, EtOH, room temp., 5 h; (b) NBS, AIBN, CCl_4, reflux, 8 h; (c) PPh_3, DMF, reflux, 3.5 h; (d) *t*BuOK, EtOH, room temp., 5 h; (e) see text; (f) triethyl phosphite, 140 °C, 4 h; (g) i. LDA, THF, –78 to 0 °C; ii **18**, 0 °C to room temp., 8 h; (h) TBAF, THF, room temp., 10 min.

phenyl)vinyl]benzene (**19**). The silyl groups in **19** were easily removed with tetrabutylammonium fluoride to form **4b**.[29] In **4b** the two double bonds have an *E* configuration.

By refluxing a mixture of substituted PcTiOs **1**–**3** and PV-diols **4a**–**c** in chloroform the axially substituted titanium phthalocyanines **5**–**7** were obtained (Scheme 1) and purified by recrystallization from methanol/chloroform (1:1). Purification by column chromatography led to decomposition.

In the ^{1}H NMR spectra of the *tert*-butyl-substituted Pcs **5a**–**c** (Scheme 1), the phthalocyanine units give a resonance pattern in the aromatic region characteristic of tetrasubstitution at the periphery of the Pc ring: Two multiplets, one between δ = 9.7 and 9.2 ppm for the eight protons in the 1,4-positions (1-H and 1′-H) and one additional multiplet between δ = 8.5 and 8.2 ppm for the four protons in the 2- or 3-positions (2-H). The 36 protons of the *tert*-butyl substituents of the Pc rings resonate at δ = 1.90–1.84 ppm as an intense and slightly broad signal due to structural isomers, which leads to slightly split singlets.

In the ^{1}H NMR spectra of Pcs **6a** and **6b** (Scheme 1), the 1-H and 1′-H signals appear as two multiplets between δ = 9.2 and 8.4 ppm. Signals from the four protons in the 2- or 3-position overlap with 16 proton signals of the peripheral phenyl fragments 3-H and 4-H with a multiplet between δ = 7.8 and 7.2 ppm. The aliphatic protons of the peripheral substituents are represented by three multiplets at $\delta \approx$ 1.9 ppm for the eight protons of the secondary methylene group, a second multiplet at $\delta \approx$ 1.5 ppm for the 24 protons of the -$C(CH_3)_2$- groups, and a third multiplet at $\delta \approx$ 0.9 ppm for the 36 *tert*-butyl protons.

The octasubstituted phthalocyanines **7a** and **7b** (Scheme 1) exhibit three signal groups: A singlet at δ = 9 ppm for the 1-H and 1′-H protons, a triplet at $\delta \approx$ 7.2 ppm for the eight 5-H protons, and a doublet at $\delta \approx$ 7.1 ppm for the 16 3-H protons.

The signals of the α-, β-, γ-, δ-, ε-, and η-protons (Scheme 1) of the axial ligands in Pcs **5**–**7** are upfield-shifted due to the ring-current effect in the phthalocyanines.

The signals of the κ-, λ-, μ-, and ν-protons are not upfield-shifted due to the longer distance from the planar Pc ring, the source of the ring-current effect. The peripheral Pc substituents do not influence very much the positions of the proton signals of the axial ligands.

The characteristic Ti=O stretching vibration in the IR spectra of Pcs **1**, **2**, and **3** at 972, 976, and 978 cm^{-1}, respectively, are absent in the IR spectra of the axially substituted Pcs **5**–**7**.

The UV/Vis maxima of the starting (phthalocyaninato)-titanium oxides **1**–**3** and the axial substituted Pcs **5**–**7** (in CH_2Cl_2) are listed in Table 1.

Table 1. Main UV/Vis absorption maxima of the Pcs **1**–**3** and **5**–**7** (solvent: dichloromethane).

	B [nm]	$Q_{1.0}$ [nm]	$Q_{0.0}$ [nm]
1	347	628	696
2	347	632	702
3	348	634	705
5a	343	632	701
5b	356	634	701
5c	347	631	701
6a	324	638	706
6b	349	637	706
7a	326	640	709
7b	340	637	707

All the axially substituted complexes are characterized by a small redshift of the Q-band with respect to the starting Pcs **1**–**3**, which is caused by the electron-donating ability of the axial ligands (Table 1). Moreover, a broadening of the Q- and B-bands is observed. The broadening and splitting of the Q-band in the spectra of **5**–**7** are caused by exciton interactions between the phthalocyanine and the axial ligand. The modification of the absorption pattern is caused by the coupling of two distinct transition dipole moments.[30–32] Exciton coupling can also cause additional absorption bands.

Pcs **5**–**7** are stable in the solid state and in solution in the dark. Semiquantitative UV/Vis measurements showed that the stability of solutions of **5**–**7**, for example, in dichloromethane, in sunlight depends on the nature of the peripheral substituents in the Pc ring and on the chain length of the axial substituents. One example of these measurements is given in Figure 1: A solution of Pc **5a** in dichloromethane was exposed to sunlight, and the UV/Vis spectra were recorded at intervals of 15–20 min.

After 200 min, the Q-band at 700 nm had decreased by a factor of around 2.4. In the case of **5b**, the Q-band decreased around three times faster. The B-band also decreased in the same manner. In all cases the Pc ring decomposes with the formation of the corresponding phthalimides.

In summary, the stability of solutions of Pcs **5**–**7** in CH_2Cl_2 for the same axial substituents increases in the order **5** < **6** < **7**. Pcs **5a**, **6a**, and **7a** with axial stilbene ligands are more stable than Pcs **5b**, **6b**, and **7b** with the longer axial chain.

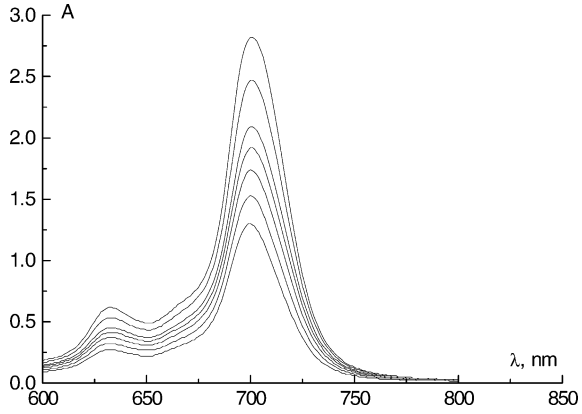


Figure 1. UV/Vis spectra of Pc **5a** in dichloromethane: Decomposition in sunlight (starting concentration 10^{-4} mol L^{-1}, illumination time 200 min).

Conclusions

To further investigate their NLO properties (optical limiting) and their use as stopcock molecules in host–guest compounds, the titanium(IV) phthalocyanines **5**–**7**, axially substituted with phenylenevinylenes of different chain lengths, have been synthesized. The syntheses were carried out by treating the (phthalocyaninato)titanium oxides **1**–**3**, which contain different peripheral substituents in the Pc ring, with the chelating PV-diols **4a**–**4c** in chloroform under reflux. It has been shown that the stability of **5**–**7** dissolved in dichloromethane in sunlight increases in the order **5** < **6** < **7** for the same axial substituents.

Experimental Section

General: Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. All solvents were dried by standard methods. $MgSO_4$ was used to dry organic solutions during workup procedures. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 percolated TLC plates. For column chromatography, silica gel 60 (230–400 mesh) was used. ^1H NMR spectra were recorded with Bruker AC 250 and 400 spectrometers. UV/Vis spectra were recorded in CH_2Cl_2 with a Lambda 25 UV/Vis spectrometer and IR spectra with a Nicolet 380 FT-IR spectrometer. Mass spectra (FAB-MS, EI, MALDI-TOF) were obtained with a Finnigan TSQ 70 MAT and a Bruker Autoflex spectrometer, and elemental analyses with a Euro EA 3000 instrument.

4-[4-(1,1,3,3-Tetramethylbutyl)phenoxy]phthalonitrile (10): A mixture of 4-(1,1,3,3-tetramethylbutyl)phenol (**9**) (9.38 g; 45.5 mmol), 4-nitrophthalonitrile (**8**) (6.06 g; 35 mmol) and K_2CO_3 (29.4 g, 213 mmol) in DMF (125 mL) was heated at 80 °C under argon. After 3 h, the reaction was completed, as checked by TLC ($CHCl_3$). The reaction mixture was cooled to room temperature, poured into icy water (1.5 L) and stirred for about 30 min. The organic phase was extracted with $CHCl_3$ (6 × 100 mL) and dried. After evaporation to dryness, the green oil obtained was crystallized. The crystals were washed with cold ethanol and dried in vacuo. Yield: 9.8 g (84%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.72 (d, ^3J = 8.4 Hz, 1 H), 7.47 (d, ^3J = 8.8 Hz, 2 H), 7.26–7.18 (m, 2 H), 6.98 (d, ^3J = 8.8 Hz, 2 H), 1.76 (s, 2 H), 1.41 (s, 6 H), 0.74 (s, 9 H) ppm. IR

(KBr): $\tilde{\nu}$ = 2956, 2904, 2232 (C≡N), 1591, 1562, 1505, 1486, 1310, 1283, 1249, 1212, 1174, 1087, 1015, 952, 878, 838, 584, 522 cm^{-1}. MS (FAB): *m*/*z* (%) = 332.2 (72) $[M]^+$, 261.1 (100) $[M - CH_2C(CH_3)_3]^+$.

Synthesis of Peripherally Substituted (Phthalocyaninato)titanium(IV) Oxides 1–3. General Procedure:[14] 4-*tert*-Butyl-, 4-[4-(1,1,3,3-tetramethylbutyl)phenoxy]- (**10**), or 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile[17] (1 equiv.), urea (0.5 equiv.) and a few drops of DBU were mixed in 1-pentanol and heated to 120 °C. At that temperature, $Ti(OBu)_4$ (0.3 equiv.) was added through a syringe, and the reaction mixtures were heated at reflux at 155 °C for 7 h. After cooling to room temperature, the mixtures were poured into methanol, and precipitation was induced by adding some water. The crude products were collected by centrifugation (or filtration) and dried in vacuo. The mixtures of metal and metal-free phthalocyanines were separated and purified by column chromatography on silica gel.

R_4PcTiO [R = OC_6H_4-*p*-$CH(CH_3)_2CH_2C(CH_3)_3$] (**2**) was obtained with 4-[4-(1,1,3,3-tetramethylbutyl)phenoxy]phthalonitrile (**10**); yield 70% as the second chromatographic fraction using CH_2Cl_2 as eluent. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.10–8.75 (m, 4×1′-H), 8.70–8.35 (m, 4×1-H), 7.78–7.36 (m, 4×2-H, 8×3-H, 8×4-H), 1.88 (d, 8×CH_2), 1.53 [t, 24×$C(CH_3)_2$], 0.91 (d, 36×*t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2951, 1601, 1505, 1475, 1397, 1365, 1331, 1234, 1176, 1117, 1071, 1014, 976 (Ti=O), 949, 872, 750, 727 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 702 (5.27), 632 (4.59), 347 (4.86), 293 (4.70) nm. MS (MALDI-TOF): *m*/*z* = 1392.7 $[M]^+$.

Metal-free phthalocyanine R_4PcH_2 [R = OC_6H_4-*p*-$CH(CH_3)_2$-$CH_2C(CH_3)_3$] was eluted as the first fraction before metal phthalocyanine **2** using CH_2Cl_2/*n*-hexane (5:2) as eluent. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.13–7.99 (m, 8 H), 7.61–7.33 (m, 20 H), 1.87 (d, 8 H), 1.50 (d, 24 H), 0.90 (d, 36 H), –0.50 (s, 2 H) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 702 (5.18), 667 (5.13), 638 (sh), 605 (sh), 341 (4.90), 289 (4.76) nm. MS (MALDI-TOF): *m*/*z* = 1330.9 $[M]^+$.

R_8PcTiO [R = OC_6H_4-3,5-$C(CH_3)_2$] (**3**) was obtained with 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile;[17] yield 62% as the second chromatographic fraction using CH_2Cl_2 as eluent. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.18 (s, 8 H), 7.26 (t, ^4J = 1.7 Hz, 8 H), 7.15 (d, ^4J = 1.7 Hz, 18 H), 1.33 (s, 144 H) ppm. IR (KBr): $\tilde{\nu}$ = 2963, 1608, 1585, 1455, 1421, 1401, 1362, 1319, 1296, 1272, 1198, 1077, 1034, 978 (Ti=O), 961, 902, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 705 (5.39), 672 (sh), 634 (4.59), 420 (4.53), 348 (4.84), 298 (4.76) nm. MS (MALDI-TOF): *m*/*z* = 2209.5 $[M]^+$.

Diethyl (4-Styrylbenzyl)phosphonate (17): Compound **17** as prepared by an Arbuzov reaction[26] with 4-(bromomethyl)stilbene (**14**)[23] (6.53 g, 23.9 mmol, 1 equiv.) and triethyl phosphite (4.2 mL, 23.9 mmol, 1 equiv.) in 51% (4.03 g) yield. MS (EI): *m*/*z* (%) = 330.1 (65) $[M]^+$, 193.2 (100), 178.2 (30). Phosphonate **17** was used immediately due to decreasing yields of the Horner–Emmons reaction after storage.

1,2-Bis(*tert*-butyldimethylsilyloxy)-4-[2-(4-styrylphenyl)vinyl]benzene (19): All used glassware was oven-dried and cooled under N_2. A solution of diisopropylamine (1.06 mL, 7.5 mmol, 2.5 equiv.) in THF (0.5 M) was cooled to –78 °C. *n*BuLi (2.64 mL, 6.6 mmol, 2.2 equiv., 2.5 M in hexane) was added through a syringe. The mixture was warmed to 0 °C for 30 min and recooled to –78 °C. Diethyl (4-styrylbenzyl)phosphonate[27] (**17**) (1 g, 3 mmol, 1.0 equiv.) as a THF solution (0.4 M) was precooled to –78 °C and transferred to the LDA solution. The reaction flask was placed in an ice bath at 0 °C, and 3,4-bis(*tert*-butyldimethylsilyloxy)benzaldehyde (**18**)[29] (1.1 g, 3 mmol, 1.0 equiv.) in THF (0.4 M) was added through a syringe and the ice bath removed. The reaction mixture was stirred at room temperature overnight, diluted with CH_2Cl_2, and washed twice with saturated aqueous $NaHCO_3$ solution followed by saturated aqueous NaCl solution. The organic layer was collected, dried, filtered, and concentrated in vacuo. The obtained product was purified by flash chromatography on silica gel using CH_2Cl_2/hexane (7:3) as eluent. Yield: 1.3 g (80%). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.53–6.77 (m, 16 H), 1.00 (s, 9 H), 0.98 (s, 9 H), 0.22 (s, 6 H) 0.20 (s, 6 H) ppm. MS (EI): *m*/*z* (%) = 542.3 (49) $[M]^+$, 485.2 (7) $[M - C_4H_9]^+$, 370.1 (15), 115.1 (36), 73.2 (100). $C_{34}H_{46}O_2Si_2$ (542.91): calcd. C 75.22, H 8.54; found C 75.22, H 8.57.

4-[2-(4-Styrylphenyl)vinyl]benzene-1,2-diol (4b): A solution of tetrabutylammonium fluoride hydrate (TBAF·$3H_2O$) (0.26 g; 0.81 mmol) in THF (1 mL) was added dropwise through a syringe to 1,2-bis(*tert*-butyldimethylsilyloxy)-4-[2-(4-styrylphenyl)vinyl]-benzene (**19**) (0.20 g; 0.37 mmol) in THF (10 mL). After 10 min, several drops of 10% AcOH/THF were added. The solvent was removed, the residue was washed with hexane and then H_2O. After drying in vacuo, the product was purified by flash chromatography on silica gel using CH_2Cl_2/ethyl acetate as eluent. Yield: 52 mg (45%). ^1H NMR (250 MHz, [D_6]DMSO): δ = 7.61–6.65 (m, 16 H) ppm. IR (KBr): $\tilde{\nu}$ = 3999 (OH), 3023, 1591, 1519, 1447, 1297, 1109, 968, 961, 821, 751, 691, 537 cm^{-1}. MS (EI): *m*/*z* (%) = 314.1 (100) $[M]^+$. $C_{22}H_{18}O_2$·$0.5H_2O$ (323.40): C 81.71, H 5.92; found: C 81.83, H 5.90.

General Procedure for the Preparation of Axially Substituted Phthalocyanines 5–7: Solutions of the substituted PcTiOs **1**–**3** (1 equiv.) and the diols **4a**–**c** (2 equiv.) in chloroform were heated at reflux for 2 h. The solvent was removed, and the crude products were recrystallized from chloroform/methanol (1:1), filtered, washed with small amounts of methanol to remove unreacted diols and dried in vacuo.

5a: Yield: 56%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.62–9.25 (m, 4×1-H, 4×1′-H), 8.46–8.31 (m, 4×2-H), 7.10–6.86 (m, 2×δ-H, 2×ε-H, 1×η-H), 6.06 (s, 2×γ-H), 5.61 (s, 1×β-H), 4.66 (s, 1×α′-H), 4.36 (s, 1×α-H), 1.89–1.86 (m, 36×*t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2950, 1736, 1613, 1484, 1394, 1365, 1326, 1281, 1256, 1201, 1151, 1077, 1014, 927, 831, 759, 694 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 701 (5.16), 632 (4.49), 343 (4.83), 275 (4.79) nm. MS (MALDI-TOF): *m*/*z* = 994.4 $[M]^+$.

5b: Yield: 62%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.65–9.33 (m, 4×1-H, 4×1′-H), 8.47–8.31 (m, 4×2-H), 7.58–6.75 (m, 2×δ-H, 2×ε-H, 2×κ-H, 2×λ-H, 2×μ-H, 1×ν-H), 6.10 (s, 2×γ-H), 5.67 (s, 1×β-H), 4.74 (s, 1×α′-H), 4.44 (s, 1×α-H), 1.94–1.77 (m, 36×*t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2952, 1600, 1503, 1472, 1395, 1367, 1330, 1234, 1176, 1114, 1072, 1014, 949, 875, 727 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 701 (5.14), 632 (4.48), 356 (4.96), 291 (4.87) nm. MS (MALDI-TOF): *m*/*z* = 1096.4 $[M]^+$.

5c: Yield: 80%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.70–9.24 (m, 4×1-H, 4×1′-H), 8.54–8.27 (m, 4×2-H), 7.0 (d, ^3J = 8.4 Hz, 2×δ-H, 2×ε-H), 6.23 (d, ^3J = 16.2 Hz, 1×γ-H), 5.98 (d, ^3J = 16.0 Hz, 1×γ-H), 5.64 (d, ^3J = 7.5 Hz, 1×β-H), 4.71 (s, 1×α′-H), 4.42 (d, ^3J = 7.5 Hz, 1×α-H), 1.84 (s, 36×*t*Bu) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 701 (5.14), 632 (4.48), 356 (4.96), 291 (4.87) nm. MS (MALDI-TOF): *m*/*z* = 1096.4 $[M]^+$.

6a: Yield: 79%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.17–8.97 (m, 4×1′-H), 8.77–8.51 (m, 4×1-H), 8.00–7.20 (m, 4×2-H, 8×3-H, 8×4-H), 7.16–6.86 (m, 2×δ-H, 2×ε-H, 1×η-H), 6.15–5.85 (m, 2×γ-H), 5.55 (d, ^3J = 7.5 Hz, 1×β-H), 4.51 (s, 1×α′-H), 4.36

(d, ^3J = 7.5 Hz, 1 × α-H), 1.89–1.83 (m, 8 × CH_2), 1.53–1.47 [m, 24 × $C(CH_3)_2$], 0.93–0.86 (m, 36 × *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2954, 2924, 1601, 1506, 1472, 1404, 1365, 1335, 1235, 1174, 1116, 1068, 1014, 952, 873, 757 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 706 (5.07), 638 (4.45), 404 (4.56), 324 (4.85), 294 (4.85) nm. MS (MALDI-TOF): *m*/*z* = 1587.2 $[M]^+$.

6b: Yield: 63%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.18–8.80 (m, 4 × 1′-H), 8.77–8.38 (m, 4 × 1-H), 7.89–6.65 (m, 4 × 2-H, 8 × 3-H, 8 × 4-H, 2 × δ-H, 2 × ε-H, 2 × κ-H, 2 × λ-H, 2 × μ-H, 1 × ν-H), 6.17–5.87 (m, 2 × γ-H), 5.57 (d, ^3J = 7.4 Hz, 1 × β-H), 4.54 (s, 1 × α′-H), 4.31 (d, ^3J = 7.4 Hz, 1 × α-H), 1.90–1.84 (m, 8 × CH_2), 1.53–1.48 [m, 24 × $C(CH_3)_2$], 0.94–0.86 (m, 36 × *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2952, 1600, 1506, 1473, 1402, 1365, 1333, 1235, 1176, 1116, 1073, 1015, 950, 827, 755 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 706 (4.99), 637 (4.38), 349 (4.90), 295 (4.83) nm. MS (MALDI-TOF): *m*/*z* = 1689.3 $[M]^+$.

7a: Yield: 72%. ^1H NMR (250 MHz, $CDCl_3$): δ = 9.10 (s, 8 × 1-H), 7.25 (t, ^4J = 1.7 Hz, 8 × 5-H), 7.13 (d, ^4J = 1.7 Hz, 16 × 3-H), 7.11–7.00 (m, 2 × δ-H, 2 × ε-H, 1 × η-H), 6.24–6.11 (m, 2 × γ-H), 5.80 (d, ^3J = 7.5 Hz, 1 × β-H), 4.89 (s, 1 × α′-H), 4.59 (d, ^3J = 7.5 Hz, 1 × α-H), 1.32 (s, 144 × *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 1607, 1585, 1457, 1421, 1403, 1362, 1317, 1295, 1272, 1199, 1078, 1034, 959, 901, 705 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 709 (5.16), 640 (sh), 420 (4.65), 326 (4.92), 299 (sh) nm. MS (MALDI-TOF): *m*/*z* = 2406.0 $[M]^+$.

7b: Yield: 59%. ^1H NMR (400 MHz, $[D_8]$THF): δ = 9.20 (s, 8 × 1-H), 7.55–7.00 (m, 8 × 5-H, 16 × 3-H, 2 × δ-H, 2 × ε-H, 2 × κ-H, 2 × λ-H, 2 × μ-H, 1 × ν-H), 6.31–6.20 (m, 2 × γ-H), 5.73 (d, ^3J = 8.0 Hz, 1 × β-H), 4.90 (s, 1 × α′-H), 4.47 (d, ^3J = 7.9 Hz, 1 × α-H), 1.32 (s, 144 × *t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 1608, 1586, 1458, 1421, 1407, 1363, 1318, 1296, 1270, 1198, 1079, 1034, 961, 902, 706 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 707 (5.17), 637 (sh), 421 (sh), 340 (4.85), 300 (4.83) nm. MS (MALDI-TOF): *m*/*z* = 2507.7 $[M]^+$.

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[1] W. Hiller, J. Strähle, W. Kobel, M. Hanack, *Z. Kristallogr.* **1982**, *159*, 173–183.
[2] H. Yonehara, H. Etori, M. K. Engel, M. Tsushima, N. Ikeda, T. Ohno, C. Pac, *Chem. Mater.* **2001**, *13*, 1015–1022.
[3] V. Gulbinas, R. Jakubenas, S. Pakalnis, A. Undzenas, *J. Chem. Phys.* **1997**, *107*, 4927–4933.
[4] K. Y. Law, *Chem. Rev.* **1993**, *93*, 449–486.
[5] P. Haisch, G. Winter, M. Hanack, L. Lüer, H. J. Egelhaaf, D. Oelkrug, *Adv. Mater.* **1997**, *9*, 316–321.
[6] G. Winter, H. Heckmann, P. Haisch, W. Eberhardt, M. Hanack, L. Lüer, H. J. Egelhaaf, D. Oelkrug, *J. Am. Chem. Soc.* **1998**, *120*, 11663–11673.
[7] J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, *Science* **1996**, *273*, 1533–1536.
[8] J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann, M. Hanack, *J. Phys. Chem. A* **2000**, *104*, 1438–1449.
[9] M. Hanack, T. Schneider, M. Barthel, J. S. Shirk, S. R. Flom, R. G. S. Pong, *Coord. Chem. Rev.* **2001**, *219–221*, 235–258.
[10] a) D. Dini, M. Barthel, M. Hanack, *Eur. J. Org. Chem.* **2001**, 3759–3769; b) M. Hanack, D. Dini, M. Barthel, S. Vagin, *Chem. Rec.* **2002**, *2*, 129–148.
[11] H. S. Nalwa, T. Saito, A. Kakuta, T. Iwayanagi, *J. Phys. Chem.* **1993**, *97*, 10515–10517.
[12] H. S. Nalwa, J. S. Shirk in *Phthalocyanines, Properties and Applications*, vol. 4 (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1996**, p. 79.
[13] M. Barthel, M. Hanack, *J. Porphyrins Phthalocyanines* **2000**, *4*, 635–638.
[14] M. Barthel, D. Dini, S. Vagin, M. Hanack, *Eur. J. Org. Chem.* **2002**, 3756–3762.
[15] a) J. Gierschner, L. Luer, D. Oelkrug, E. Musluoglu, B. Behnisch, M. Hanack, *Adv. Mater.* **2000**, *12*, 757–761; b) K. Komorowska, S. Brasselet, G. Dutier, I. Ledoux, J. Zyss, L. Poulsen, M. Jazdzyk, H.-J. Egelhaaf, J. Gierschner, M. Hanack, *J. Chem. Phys.* **2005**, *318*, 12–20.
[16] L. Poulsen, M. Jazdzyk, J.-E. Communal, J. C. Sancho-Garcia, A. Mura, G. Bongiovanni, D. Beljonne, J. Cornil, M. Hanack, H.-J. Egelhaaf, J. Gierschner, *J. Am. Chem. Soc.* **2007**, *129*, 8585–8593.
[17] M. J. Plater, A. Jeremiah, G. Bourhill, *J. Chem. Soc. Perkin Trans. 1* **2002**, 91–96.
[18] a) N. M. Cullinane, *J. Chem. Soc.* **1923**, *123*, 2053–2060; b) J.-Y. Lee, W.-J. Lee, C. S. Baek, H.-B. Bang, *Bull. Korean Chem. Soc.* **2004**, *25*, 1941–1944.
[19] M. A. Ali, K. Kondo, Y. Tsuda, *Chem. Pharm. Bull.* **1992**, *40*, 1130–1136.
[20] K.-H. Schweikart, M. Hanack, L. Lüer, D. Oelkrug, *Eur. J. Org. Chem.* **2001**, 293–302.
[21] a) K.-H. Schweikart, M. Hanack, L. Lüer, D. Oelkrug, *Eur. J. Org. Chem.* **2001**, 293–302; b) L. Zhou, L. Wang, *Synthesis* **2006**, *16*, 2653–2658; c) C. Wang, L. Yan, Z. Zheng, D. Yang, Y. Pan, *Tetrahedron* **2006**, *62*, 7712–7717; d) O. Aksin, H. Turkmen, L. Artok, B. Cetinkaya, C. Ni, O. Buyukgungor, E. Ozkal, *J. Organomet. Chem.* **2006**, *691*, 3027–3036.
[22] a) T. Xiao, Q. Ye, L. Sun, *J. Phys. Chem. B* **1997**, *101*, 632–638; b) A. Watakabe, H. Okada, T. Kunitake, H. Okada, T. Kunitake, *Langmuir* **1994**, *10*, 2722–2726; c) S. Misumi, M. Kuwana, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1962**, *35*, 135–142.
[23] T. W. Campbell, R. N. McDonald, *J. Org. Chem.* **1959**, *24*, 1246–1251.
[24] A. E. Siegrist, P. Liechti, H. R. Meyer, K. Weber, *Helv. Chim. Acta* **1969**, *52*, 2521–2554.
[25] B. A. Arbuzov, *Pure Appl. Chem.* **1964**, *9*, 307–335.
[26] C. C. Kwok, M. S. Wong, *Chem. Mater.* **2002**, *14*, 3158–3166.
[27] W. Wadsworth, *Org. React.* **1977**, *25*, 73–253.
[28] a) M. Uchiyama, H. Ozawa, K. Takuma, Y. Matsumoto, M. Yonehara, K. Hiroya, T. Sakamoto, *Org. Lett.* **2006**, *8*, 5517–5520; b) N. J. Lawrence, D. Rennison, A. T. McGown, J. A. Hadfield, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3759–3763; c) M. Femenia-Rios, C. M. Garcia-Pajon, R. Hernandez-Galan, A. J. Macias-Sanchez, I. G. Collado, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5836–5839.
[29] G. N. Tew, M. U. Pralle, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 9852–9866.
[30] N. Kobayashi, A. Muranaka, K. Ishii, *Inorg. Chem.* **2000**, *39*, 2256–2257.
[31] C. A. Hunter, J. K. M. Sanders, A. J. Stone, *Chem. Phys.* **1989**, *133*, 395–404.
[32] F. London, *J. Phys. Chem.* **1942**, *46*, 305–316.

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