Inorganica Chimica Acta 374 (2011) 119–126

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and crystal structure of novel, soluble titanyl phthalocyanines

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ARTICLE INFO

Article history:
Available online 4 February 2011

Dedicated to Professor Dr. Wolfgang Kaim on the occasion of his 60th birthday.

Keywords:
Titanyl phthalocyanine
Crystal structure
UV–Vis spectroscopy
NMR spectroscopy

ABSTRACT

Novel titanyl phthalocyanines titanyl-tetrakis-(1,1,4,4-tetramethyl-6,7-tetralino)-porphyrazine (**1**), titanyl-2,3,9,10,16,17,23,24-octakis(phenylethynyl)-phthalocyanine (**2a**), titanyl-2,3,9,10,16,17,23,24-octakis((4-*tert*-butylphenyl)ethynyl)-phthalocyanine (**3a**), titanyl-(2,3,9,10,16,17,23,24-octakis(phenylethyl))-phthalocyanine (**2b**) and titanyl-(2,3,9,10,16,17,23,24-octakis((4-*tert*-butylphenyl)ethyl)-phthalocyanine (**3b**) were prepared by reductive cyclotetramerisation of the respective dinitrile precursors in the presence of a titanium(IV) template. The spectroscopic properties were examined by UV–Vis and IR techniques. Soluble compounds **1**, **2b** and **3b** were characterized by ^{1}H and ^{13}C NMR spectroscopy and show good stability towards thermal degradation. The molecular structure of **1** was determined, thus being one of the few examples of soluble phthalocyanines with a low grade of aggregation characterized by single crystal X-ray diffraction. Compound 1 crystallizes in the triclinic space group $P\bar{1}$, and the molecules arrange in a coplanar, slipped-stacked structure.

1. Introduction

Metal free phthalocyanine PcH_2 is a porphyrinoid macrocycle prepared by reductive tetramerization of four phthalonitrile units [1–3]. The valence structure of phthalocyanine was first recognized by Linstead et al. in 1934 [4]. Since then, metal phthalocyanines [PcM] have been described for most metals. The extended 18π electron aromatic system, its non-innocent ligand character ($Pc^{2-/1-}$) and last but not least the lattice-packing in the solid state are responsible for physical characteristics, such as the intense colour and chemically, thermally or light induced semi-conducting properties of these dyes. Due to π-stacking unsubstituted phthalocyanines are insoluble in common organic solvents which limits the processability, derivatisation and the characterization of this class of compounds [1–3]. By introduction of bulky substituents at the ligand periphery intermolecular interaction of the π systems can be reduced, phthalocyanines become soluble and ^{13}C NMR spectra are available in common organic solvents. As a consequence, a variety of phthalodinitriles bearing alkyl, alkoxy and other functional groups have been synthesized and employed in cyclotetramerization reactions [2,5]. While template reactions of mono-substituted dinitriles typically lead to mixtures of regioisomers [R_1PcM], bis-substituted dinitriles, depending on the substitution pattern, can lead to uniform D_{4h} symmetrical compounds [1,4-R_2PcM] or [2,3-R_2PcM] (Fig. 1).

The parent titanyl phthalocyanine, [PcTiO] [6,7] and its ring-substituted alkyl or alkoxy derivatives [R_nPcTiO] [8,9] have found application in many fields of light driven processes such as in the manufacture of non-toxic organic photoconductors in electrographic printing devices [10], in CD-R optical data storage [11], and as optical limiting materials [12]. The evaluation of the solid state structure of titanyl phthalocyanines is essential, as different arrangement of these molecules in the lattice structure of polymorphic forms influences the optoelectronic properties of [PcTiO] [13–15]. However, while the effect of equatorial *n*-alkyl substitution on solubility, on UV–Vis characteristics and photostability has previously been reported by Hanack et al. [9,16–18], no crystal structure of a soluble titanyl phthalocyanine has been published so far. With respect to the large number of soluble phthalocyanines, surprisingly little is known on their molecular and lattice structures in general [19–22]. The presence of either isomeric mixtures and/or disorder in long-chain alkyl substituents tends to prevent single crystal XRD analyses. As an extension of our studies on partly soluble parent titanium phthalocyanines with axial sulfido, imido, phenylendiamido and ureato ligands [23–25] we became interested to design and fully characterize isomerically pure octasubstituted soluble titanyl phtalocyanines which are expected to be air stable, suitable for spin coating of surfaces, and for derivatisation of the axial oxo ligand.

As synthetic strategy we decided to use alkynyl substituted dinitriles **5a** and **6a** prepared via Sonogashira coupling [26] as well as the reduced alkyl analogues **5b** and **6b** (Fig. 2). Compounds **5a** and **5b** have been employed by Leznoff et al. to obtain the corresponding metal free phthalocyanines [27] as well as unsymmetrical push–pull-macrocycles [28]. As the synthesis of **5a**, **5b**, **6a** and **6b** involves metal-catalyzed reactions which are difficult to handle in large scale, we decided to also employ

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doi:10.1016/j.ica.2011.01.099

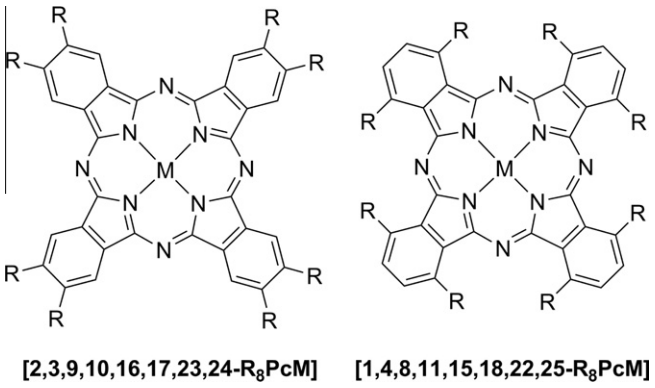


Fig. 1. Substituted D_{4h} symmetrical metal phthalocyanine.

6,7-dicyano-1,1,4,4-tetramethyltetraline (**4**) as starting material. Luk'yanets et al. used **4** in the preparation of metal-free tetra-(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine and corresponding zinc, copper, vanadyl and cobalt complexes [29–31]. We hoped that cyclic alkyl substituents are more rigid than non-cyclic ones, which should facilitate crystallization and enhance stability of these titanyl phthalocyanines.

2. Experimental

2.1. General procedures

Dinitriles **4** [29,32,33], **5a** [26,34] and **6a** [26,34] were prepared according to literature procedures. Compound **4** was purified by column chromatography (silica gel, CH_2Cl_2) prior to use. Chloronaphthalene was obtained from Acros as a mixture of 1-chloronaphthalene (90%) and 2-chloronaphthalene (10%). Chloronaphthalene and 1-octane were dried with CaH_2, distilled and stored over molecular sieves (4 Å). $TiCl_4$ and Ti(O*n*Bu)$_4$ were obtained from Acros and stored under inert gas. Pd/C (10%) was obtained from Merck. Preparations were carried out under dry argon atmosphere using standard Schlenk or glove box techniques.

The electronic spectra were recorded on a Shimadzu UV-1601 PC spectrophotometer. IR spectra were recorded on a Bruker IFS 588 spectrometer. EI mass spectra were taken on a Finnigan MAT95 spectrometer (E = 70 eV). APCI mass spectra were taken on a Finnigan LTQ-FT spectrometer using dichloromethane as solvent. MALDI-TOF mass spectra were taken on a Bruker Biflex III using pyrene as matrix. Elemental analyses of C, H and N elements was carried out using an Elementar Vario EL. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 500. Thermal gravimetric analyses (TGA) were carried out using a TGA/SDTA 851, Mettler. The heating range was from 25 to 800 °C with a heating rate of 10 °C min^{-1}.

2.2. 4,5-Bis(phenylethyl)phthalodinitrile (*5b*)

Three hundred milligrams of 4,5-bis(phenylethynyl)phthalodinitrile **5a** (0.91 mmol, 1.00 equiv) was dissolved in 20 mL of ethyl acetate. Ninety-one milligrams of Pd/C (10%) were added. The reaction flask was purged with H_2 and the mixture was stirred under H_2 atmosphere (1 bar) at room temperature for 48 h. The catalyst was removed by filtration and the volatiles were removed under reduced pressure. The resulting brown solid was washed with hexane, recrystallized from methanol and dried under vacuum. Yield: 268 mg, 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41 (s, 2H), 7.13–7.25 (m, 6H), 7.00 (d, $^3J_{HH}$ = 6.7 Hz, 4H), 2.84–2.89 (m, 4H), 2.75–2.80 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.3, 139.9, 134.4, 128.8, 128.4, 126.8, 115.7, 113.3, 36.5, 34.4 ppm. EI-HRMS$^+$ *m/z* (%) = 336.1639 (100) [M$^+$], $C_{24}H_{20}N_2$ requires 336.1626 (100).

2.3. 4,5-Bis(4-tert-butylphenylethyl)phthalodinitrile (*6b*)

4,5-Bis((4-*tert*-butylphenyl)ethynyl)phthalodinitrile **6a** (1.09 g, 2.47 mmol, 1.00 equiv) were dissolved in 30 mL of ethyl acetate. One hundred and fifty milligrams of Pd/C (10%) were added. The reaction flask was purged with H_2 and the mixture was stirred under H_2 atmosphere (1 bar) at room temperature for 48 h. The catalyst was removed by filtration and the volatiles were removed under reduced pressure. The brown solid was washed with hexane, recrystallized from methanol and dried under vacuum. Yield: 937 mg, 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.48 (s, 2H), 7.32 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.02 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 2.91–2.94 (m, 4H), 2.79–2.85 (m, 4H), 1.31 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.9, 146.4, 136.8, 134.4, 128.2, 125.7, 115.8, 113.3, 36.0, 34.6, 34.5, 31.5 ppm. EI-HRMS$^+$ *m/z* (%) = 448.2867 (87) [M$^+$], $C_{32}H_{36}N_2$ requires 448.2878 (100).

2.4. Titanyl-tetrakis-(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine (*1*)

A mixture of 5.23 g of **4** (21.95 mmol, 4.15 equiv), 700 mg of urea (11.66 mmol, 2.20 equiv) and 1.80 g of Ti(O*n*Bu)$_4$ (5.29 mmol, 1.00 equiv) in 4.5 mL of 1-octanol was stirred for 6 h in a pre-heated oil bath at 150 °C. The reaction mixture turned dark green. After cooling, 60 mL of methanol were added and the mixture was stirred at 60 °C for 30 min. The resulting green powder was collected by filtration and successively extracted with methanol and hexane. The product was dried under vacuum at 150 °C. Yield: 1.70 g, 32%. Crystals suitable for X-ray diffraction were obtained from a saturated solution in $CHCl_3$ in the dark. *Anal.* Calc. for $C_{64}H_{72}N_8TiO$ (1017.18 g/mol): C, 75.35; H, 7.41; N, 10.98. Found: C, 74.51; H, 7.21; N, 11.02%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.62 (s, 8H), 2.08 (s, 16H), 1.89 (s, 24H), 1.81 (s, 24H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.2, 149.4, 135.0, 121.9, 36.1, 35.4, 33.0, 32.8 ppm. IR ν = 2959(s), 2922(s), 2860(m), 1616(w), 1493(m),

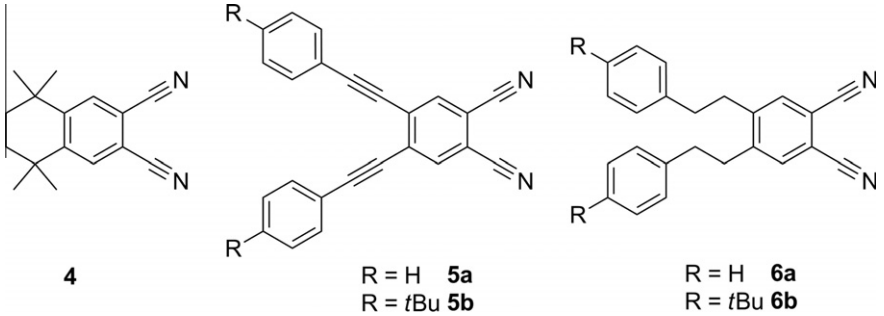


Fig. 2. Dinitriles investigated in this study.

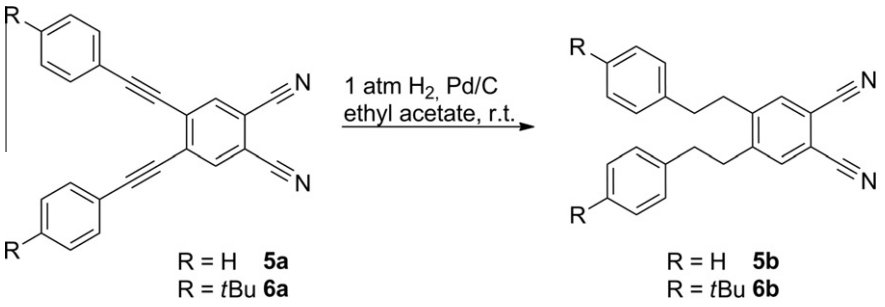
1320(s), 1306(s), 1188(w), 1113(w), 1071(s), 977(m, $\nu_{Ti=O}$), 870(m), 763(w), 753(w), 708(m) cm^{-1}. UV–Vis (CH_2Cl_2) λ = 713(s), 683(sh), 641(w), 348(m), 237(m) nm. MALDI-TOF-MS^+ m/z = 1017 [M^+], APCI-$HRMS^+$ m/z = 1071.5380 [M^++H], $C_{64}H_{73}N_8TiO$ requires 1017.5383.

2.5. Titanyl-2,3,9,10,16,17,23,24-octakis(phenylethynyl)-phthalocyanine (**2a**)

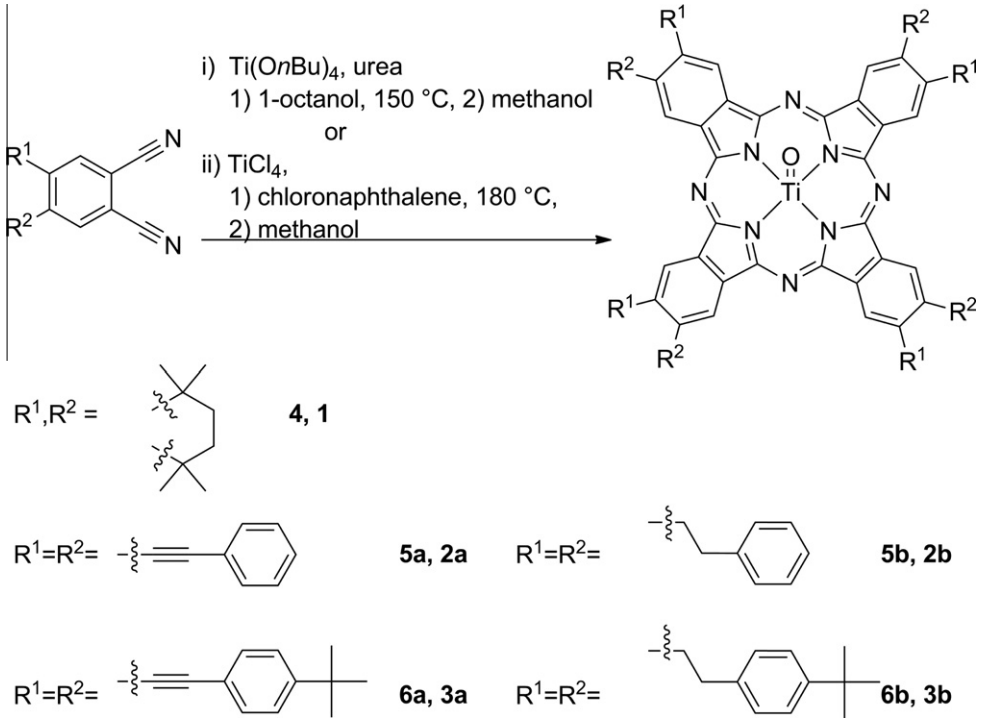
A mixture of 600 mg of **5a** (1.83 mmol, 4.00 equiv), 55 mg of urea (0.92 mmol, 2.00 equiv) and 171 mg of Ti(O*n*Bu)$_4$ (0.50 mmol, 1.00 equiv) in 5 mL of 1-octanol was stirred for 5 h in a pre-heated oil bath at 150 °C and then at 100 °C overnight. The reaction mixture turned dark green. The green solid was precipitated by adding 60 mL of methanol and successively extracted with methanol, acetonitrile, hexane and diethyl ether. The product was dried under vacuum. Yield: 500 mg, 72%. *Anal.* Calc. for $C_{96}H_{48}N_8OTi$ (1377.33 g/mol): C, 83.71; H, 3.51; N, 8.14. Found: C, 80.09; H, 3.70; N, 7.60%. IR ν = 1596(w), 1544(w), 1492(m), 1442(w), 1401(w), 1317(w), 1276(w), 1205(w), 1147(w), 1072(s), 969 (w, $\nu_{Ti=O}$), 897(w), 881(w), 827(w), 750(s), 686(s), 530(w), 483(w), 454(w) cm^{-1}. UV–Vis (chloronaphthalene) λ = 751(m), 678(w), 388(s) nm. MALDI-TOF-MS^+ m/z = 1377 [M^+].

2.6. Titanyl-2,3,9,10,16,17,23,24-octakis((4-tert-butylphenyl)-ethynyl)-phthalocyanine (**3a**)

A mixture of 400 mg of **6a** (0.91 mmol, 4.00 equiv), 28 mg of urea (0.46 mmol, 2.00 equiv) and 79 mg of Ti(O*n*Bu)$_4$ (0.23 mmol, 1.00 equiv) in 5 mL of 1-octanol was stirred overnight in a pre-heated oil bath at 180 °C. The reaction mixture turned dark green. The green solid was precipitated by adding 60 mL of hexane and successively extracted with methanol, acetonitrile, hexane and diethyl ether. The product was dried under vacuum. Yield: 200 mg, 48%. *Anal.* Calc. for $C_{128}H_{112}N_8OTi$ (1826.18 g/mol): C, 84.19; H, 6.18; N, 6.14. Found: C, 82.73; H, 6.70; N, 5.80%. IR ν = 2956(s), 2904(m), 2866(m), 2207(m), 1772(m), 1709(s), 1604(m), 1504(m), 1363(m), 1310(m), 1265(m), 1074(s), 1014(m), 828(s), 741(m), 560(m) cm^{-1}. UV–Vis (chloronaphthalene) λ = 759(s), 682(m), 642(m) nm. MALDI-TOF-MS^+ m/z = 1827 [M^+].



Scheme 1. Reduction of dinitriles **5a** and **6a**.



Scheme 2. Synthesis of **1**, **2a** and **3a** (method i), and **2b** and **3b** (method ii).

2.7. Titanyl-2,3,9,10,16,17,23,24-octakis(phenylethyl)phthalocyanine (**2b**)

Four hundred and forty-one milligrams of **5b** (1.31 mmol, 3.00 equiv) were dissolved in 5 mL of chloronaphthalene at room temperature. Eighty-three milligrams of $TiCl_4$ (0.44 mmol, 1.00 equiv) were added and the mixture was stirred for 4 h in a pre-heated oil bath at 180 °C and then at 100 °C overnight. The reaction mixture turned dark green. A green solid was precipitated with 30 mL of hexane and successively extracted with methanol, acetonitrile, hexane and diethyl ether. The product was dried under vacuum. Yield: 380 mg, 61%. *Anal.* Calc. for $C_{96}H_{80}N_8OTi$ (1409.58 g/mol): C, 78.73; H, 5.51; N, 7.65. Found: C, 75.66; H, 5.81; N, 7.34%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 9.06 (s, 8H), 7.35 (br, 40H), 3.27–3.42 (br, 32H) ppm. IR ν = 2950(m), 2603(m), 2497(m), 1475(m), 1444(m), 1397(m), 1362(m), 1329(m), 1267(w), 1172(w), 1078(s), 1036(s), 972(w, $\nu_{Ti=O}$), 818(m), 748 (w), 557 (m) cm^{-1}. UV–Vis (chloronaphthalene) λ = 712(s), 677(w), 643(w) nm. MALDI-TOF-MS$^+$ *m/z* = 1410 [M$^+$].

2.8. Titanyl-2,3,9,10,16,17,23,24-octakis((4-tert-butylphenyl)ethyl)-phthalocyanine (**3b**)

One hundred milligrams of **6b** (0.22 mmol, 3.00 equiv) were dissolved in 2 mL of chloronaphthalene at room temperature. Fourteen milligrams of $TiCl_4$ (0.07 mmol, 1.00 equiv) were added and the mixture was stirred for 4 h in a pre-heated oil bath at 180 °C. The reaction mixture turned dark green. A green solid was precipitated and successively extracted with methanol, acetonitrile, hexane and diethyl ether. The product was dried under vacuum. Yield: 60 mg, 44%. *Anal.* Calc. for $C_{96}H_{80}N_8OTi$ (1858.43 g/mol): C, 80.35; H, 7.59; N, 5.86. Found: C, 78.29; H, 7.23; N, 5.51%. ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 8.75 (s, 8H), 7.21–7.29 (m, 32H), 3.05–3.24 (br, 32H), 1.24 (s, 72H) ppm. ^{13}C NMR (75 MHz, THF-d_8) δ = 150.6, 148.1, 143.1, 138.5, 135.0, 127.6, 124.8, 122.5, 36.7, 35.6, 33.7, 30.6 ppm. IR ν = 2602(w), 2497(w), 1600(w), 1493(m), 1449(m), 1398(m), 1326(s), 1078(s), 965(m, $\nu_{Ti=O}$), 747(m), 727(m), 694 (s) cm^{-1}. UV–Vis (chloronaphthalene) λ = 710(s), 682(w), 642(m) nm. MALDI-TOF-MS$^+$ *m/z* = 1859 [M$^+$].

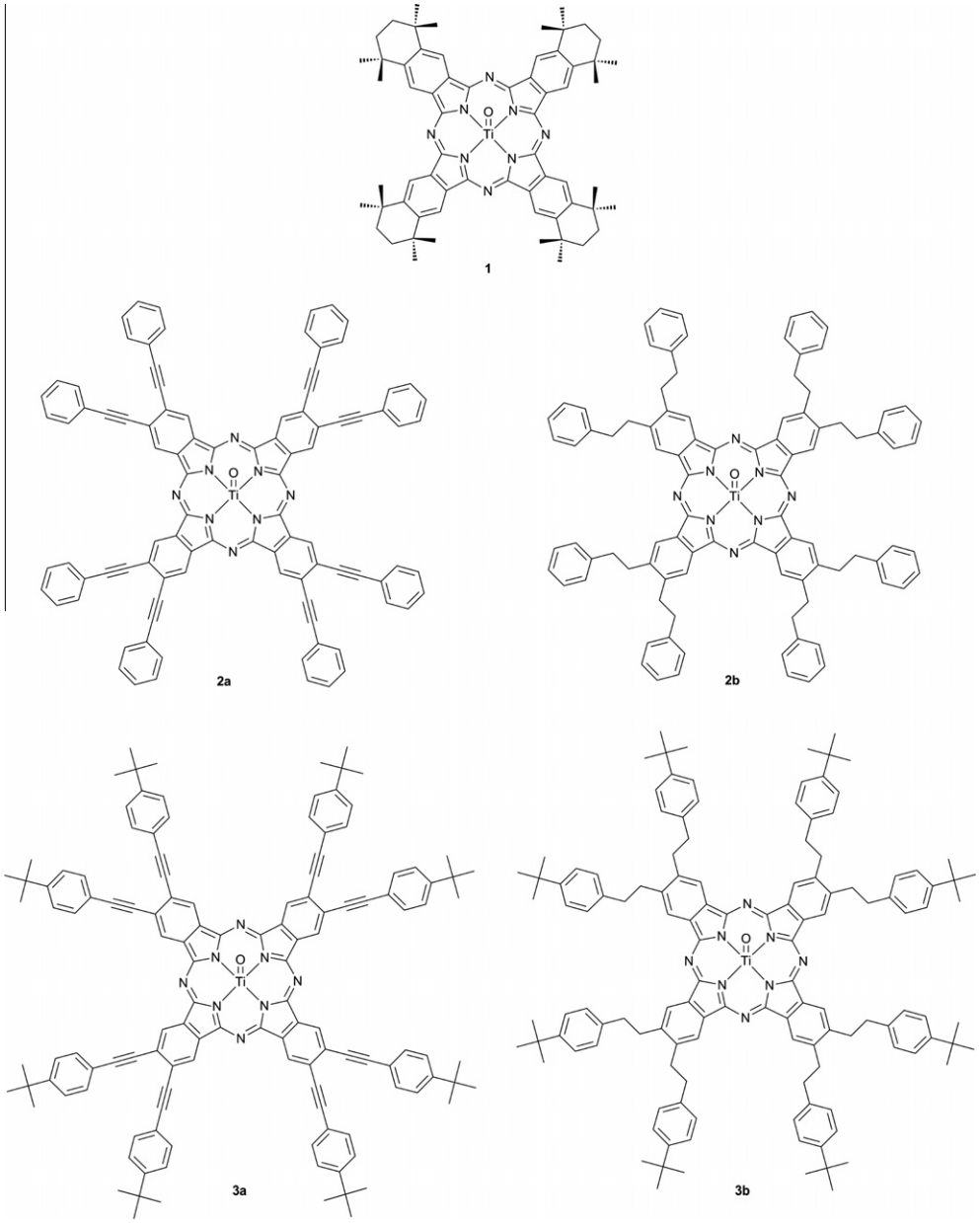


Fig. 3. Prepared titanyl phthalocyanines.

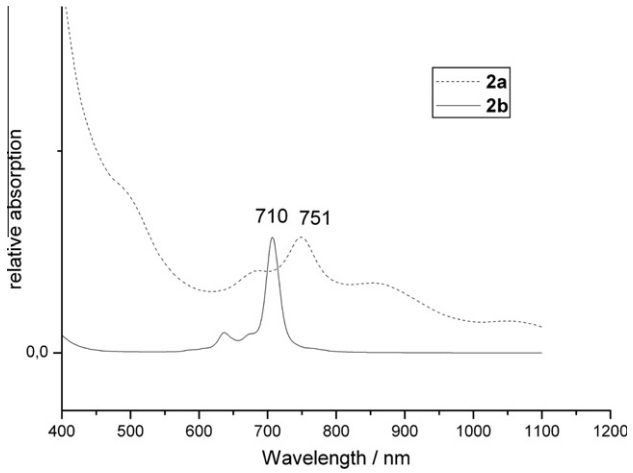


Fig. 4. Comparison of UV–Vis spectra of **2a** and **2b** in chloronaphthalene.

3. Results and discussion

3.1. Preparation

The dinitriles **4** [29,31], **5a** and **5b** [26] were prepared according to the literature procedures. The reduced dinitriles **5b** and **6b** were prepared from **5a** and **6a** in an analogous manner to the preparation of 3,6-dialkyl substituted dinitriles reported by Hanack et al. [35]. The reaction of the alkynyl substituted dinitriles with 1 atm H_2 and Pd/C in ethyl acetate afforded the desired products in 85–88% yield (Scheme 1).

Unsubstituted titanyl phthalocyanine [PcTiO] can be synthesized by reaction of phthalonitrile with $TiCl_3$ [6], $TiCl_4$ [7] or Ti(O*n*-Bu)$_4$ [36] in high-boiling solvents. Analogously, **1**, **2a** and **3a** were prepared by the reaction of 4.00–4.15 equiv of the respective dinitrile, 1.00 equiv Ti(O*n*Bu)$_4$ and 2.00–2.20 equiv urea in 1-octanol at 150 °C (Scheme 2) and subsequent methanolysis. In the case of alkyl substituted dinitriles **5b** and **6b**, this strategy did not afford the desired macrocycles. Therefore, the preparations of **2b** and **3b** were carried out in chloronaphthalene at 180 °C using $TiCl_4$ as metal template. The products were obtained in 32–72% yield, and the yields decrease as the solubility of the resulting phthalocyanines increases (Fig. 3). The intensely green products were characterized by MS, elemental analysis and spectral properties. Compounds **1** and **3b** are soluble in organic solvents such as dichloromethane, chloroform, benzene or THF. Compound **2b** shows moderate solubility in dichloromethane and THF. Complexes of the rigid planar ligands **2a** and **3a** are insoluble in common organic solvents.

3.2. Spectroscopy and TGA

The insolubility of **2a** and **3a** does not allow characterization via NMR spectroscopy. In **2b** the flexible ethanediyl linkers enhance the solubility, so that ^{1}H NMR spectra could be recorded in CD_2Cl_2. Compounds **1** and **3b** show the best solubility, so that even well resolved ^{13}C NMR spectra could be obtained (see Supporting information). In all ^{1}H NMR spectra, the characteristic downfield shift of the Pc protons is observed, as they appear as singlets between 8.75 and 9.62 ppm. This is due to the strong ring current effect in the aromatic macrocycles [26,37]. Due to the symmetry of **1**, the ^{1}H NMR spectrum in $CDCl_3$ shows only four singlets (see Supporting information). The signal observed at 9.62 ppm refers to the eight aromatic protons. The aliphatic protons are observed between 1.81 and 2.08 ppm. The methyl groups appear as a set of two singlets which is not observed in compounds without axial ligands such as the free ligand tetrakis-(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine. This effect can be explained by the lowering of the molecular symmetry imposed by the axial Ti=O group. The upper and lower hemisphere of the macrocycle become inequivalent and the methyl groups pointing towards the titanyl moiety (*endo*) and those pointing away (*exo*) are located in different chemical environments. This is also supported by the molecular structure of **1**.

The UV–Vis spectrum of **1** in dichloromethane shows the typical Q- and B-band absorptions for metal phthalocyanines (see Supporting information). The relative absorption maxima (713, 348 and 237 nm) compare well with the values reported by Luk'yanets et al. for the analogous C_{4v} symmetric vanadyl-tetrakis-(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine (716 and 353 nm) [29,31]. The Q-band is shifted bathochromically compared to the D_{4h} symmetric zinc, copper and cobalt compounds (691, 691 and 682 nm, respectively) and the C_{2v} symmetric protonated ligand (712 and 678 nm).

A comparison of the UV–Vis spectra of **2a** and **2b** shows the effect of solubility and the nature of peripheral substituents on the spectroscopic properties (Fig. 4). Due to the poor solubility of **2a** the Q-band is much broader than in **1** or **2b**. Also, the extinction maximum is shifted bathochromically because of the conjugation

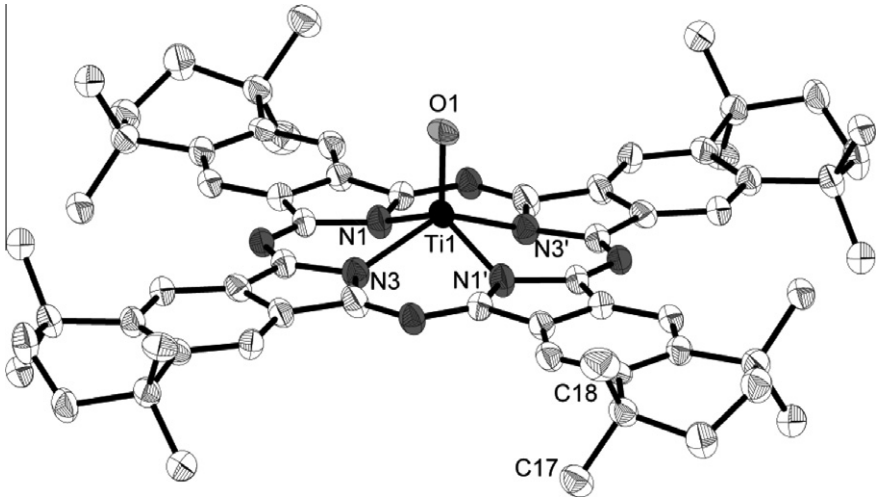


Fig. 5. Molecular structure of **1**. Ellipsoids are shown at 50% probability. H atoms, disorder of the Ti=O moiety and solvent molecules are omitted for clarity.

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$C_{67}H_{75}Cl_9N_8OTi$
Formula weight (g/mol)	1375.30
Temperature (K)	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.4678(15)
b (Å)	12.4707(16)
c (Å)	12.9692(18)
α (°)	112.400(10)
β, (°)	109.897(10)
γ (°)	99.122(10)
V (Å^3)	1653.9(4)
λ (Å)	Mo Kα, 0.71073
Z	1
$D_{Calc.}$ (mg/m^3)	1.381
μ (mm^{-1})	0.542
Crystal size (mm)	0.33 × 0.15 × 0.09
2θ Range (°)	1.84–27.29
Reflections collected	35 525
Data/restraints/parameters	35 525/63/452
Goodness-of-fit on F^2	0.824
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0976, 0.2501
R_1[a], wR_2[b] (all data)	0.2084, 0.2912

[a] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$.
[b] $wR_2 = \{[\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}\}$.

Table 2
Selected bond distances (Å) and angles (°) of **1**.

Ti1–O1	1.619(8)
Ti1–N1	2.139(9)
Ti1–N3	2.112(1)
N1–Ti–O1	111.0(5)
N1–Ti1–N1′	138.4(4)
N3–Ti1–O1	112.3(5)
N1–Ti1–N3	82.7(3)
N3–Ti1–N3′	138.3(3)

of the macrocyclic core and the ethynyl linkers. A similar bathochromic shift is observed for naphthalocyanines compared to analogous phthalocyanines [38]. The extension of the aromatic system was found to causes a shift of the Q-band maximum of about 70–90 nm. In our case, the exchange of an ethanediyl for an ethynediyl linker causes a bathochromic shift of about 40 nm.

The IR spectra of all compounds display absorptions representing the organic ligand and the band characteristic for the $\nu_{Ti=O}$ stretching mode at around 970 cm^{-1} [26].

The group of Hanack found that long chain *n*-alkyl and *n*-alkoxy substituted titanyl phthalocyanines cannot be sublimed in high vacuum without thermal degradation [9]. For this reason, these compounds could not be applied in physical vapour deposition experiments which are used to prepare ordered mono- or multilayers of metal Pc's. Therefore we conducted TGA measurements to investigate the thermal robustness of our compounds (see Supporting information). Thermal degradation (1% weight loss) starts at temperatures higher than 400 °C for both, the fully conjugated alkynyl **2a** and the cyclic alkyl derivatives and **1**, whereas non-cyclic alkyls **2b** and **3b** start to decompose above 300 °C. This thermal stability of **1** and **2a** in combination with a low grade of aggregation of **1** in particular makes the latter an interesting target for physical vapour deposition experiments. We attribute this stability to the fact that incorporation of long and thermally labile *n*-alkyl chains into the complex has been avoided without loosing the substituents' property to inhibit aggregation.

3.3. Crystal structure of *1*

Crystals for X-ray diffraction were obtained from a saturated chloroform solution. Solutions of alkyl substituted titanyl phthalocyanines often slowly decompose when exposed to light and oxygen, resulting in an orange solution and a white precipitate [9]. Thus, the complexes have to be kept from light and air during crystallization. **1** crystallizes in the triclinic space group $P\bar{1}$ (a = 12.4678(15) Å, b = 12.4707(16) Å, c = 12.9692(18) Å, α = 112.400(10)°, β = 109.897(10)°, γ = 99.122(10)°) with one molecule in the unit cell. Crystal data and refinement parameters for **1** are given in Table 1. Fig. 5 shows the molecular structure of the molecule possessing a crystallographic inversion centre. The titanyl moiety is disordered within the ligand pocket with an equal occupancy of both positions. It creates a dome over the isoindoline N

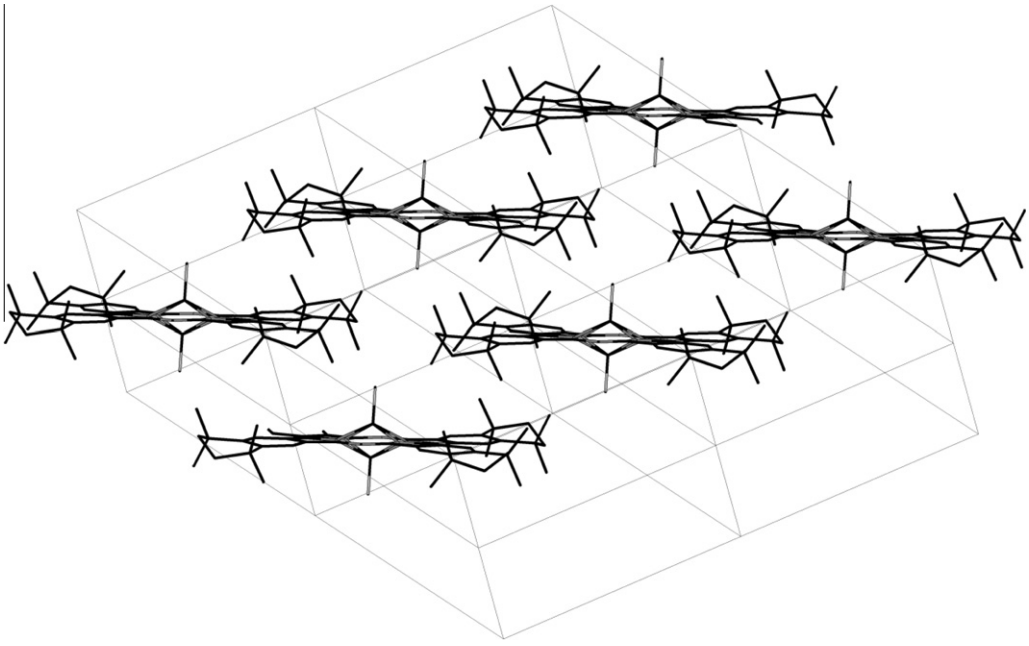


Fig. 6. Molecular packing of **1**, view along the Pc layers. Both orientations of the disordered Ti=O moiety are displayed. H atoms and three disordered molecules of chloroform per **1** are omitted for clarity.

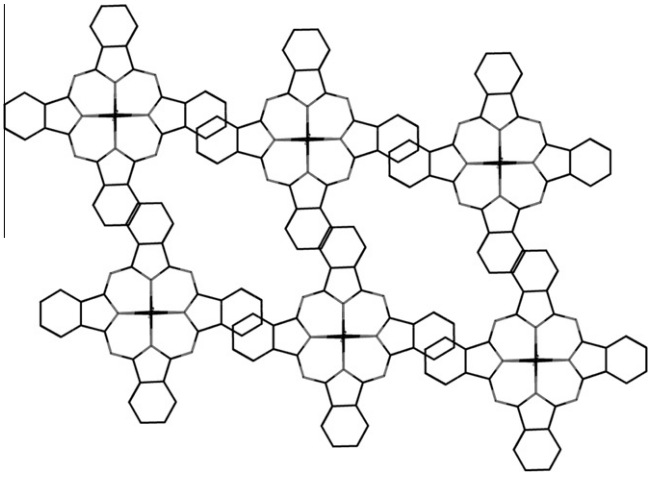


Fig. 7. Molecular packing of **1**, view along the Ti=O bond. Ligand periphery, H atoms and molecules of chloroform are omitted for clarity.

atoms. The distance between the titanium atom and the plane defined by N1, N1′, N3 and N3′ is 0.748(3) Å. The macrocycle slightly deviates from planarity, adapting a 'saddle' conformation [19]. In [PcTiO], a 'saucer' conformation is present [15]. The difference in the chemical environment of the *endo* and *exo* methyl groups is represented by the different distances O1–C18 (8.67(1) Å) and O1–C17 (9.03(0) Å). The bond distances Ti1–O1 (1.619(8) Å), Ti1–N1 (2.139(9) Å) and Ti1–N3 (2.112(1) Å) as well as the angles N1–Ti1–O1 (111.0(5)°) and N3–Ti1–O1 (112.3(5)°) are comparable to those reported for the unsubstituted complex [PcTiO] [15]. Selected bond distances and angles are summarized in Table 2.

The lattice structure of **1** is shown in Figs. 6 and 7. Three disordered molecules of chloroform are located between the macrocycle layers and are omitted for clarity. The orientation of the titanyl moiety is disordered due to the steric bulk induced by the peripheral methyl groups, since no disorder occurs in unsubstituted [PcTiO]. The macrocycles are oriented essentially coplanar in a slipped-stacked manner [19]. The distances between the titanium atoms of two neighbouring macrocyles are 12.471(4) Å and 12.468(4) Å, respectively. This distance is significantly longer than in unsubstituted [PcTiO] ($d_{average}$ = 6.701 and 9.720 Å for the two polymorphs) [15]. The distances between the ligand layers (plane through N1, N1′, N3 and N3′) are 9.800 and 9.652 Å and lie between the values for the two polymorphs reported by Hiller et al. ($d_{average}$ = 4.879 and 12.281 Å, respectively). The aromatic systems of neighbouring macrocycles overlap partially (Fig. 7), but the overlapping area is much smaller than in the crystal phases 1 and 2 of [PcTiO] [13]. This should be a crucial factor regarding the semiconducting and photophysical properties of **1**. It is known from fluorescence spectroscopy that the excited state lifetime of phthalocyanines decreases with an increase of aggregation between the molecules, as non-radiative excited state quenching occurs [39–43]. This has hampered the application of Pc's in dye sensitized solar cells [39,40]. The structure of **1** shows that by introduction of the annellated cyclohexene moiety the aggregation in solid state could be minimized, and hence less intermolecular fluorescence quenching can be expected.

4. Conclusions

Novel titanyl phthalocyanines **1**, **2a**, **2b**, **3a** and **3b** have been synthesized by cyclotetramerization of the respective dinitrile precursors using Ti(O*n*Bu)$_4$ or TiCl$_4$ as template. While the alkynyl substituted compounds **2a** and **3a** are insoluble, alkyl substituted **1**, **2b** and **3b** show good solubility in organic solvents. These compounds have been characterized by NMR and UV–Vis spectroscopy and they show enhanced thermal stability compared to *n*-alkyl substituted Pc's. Therefore the benefits of solubility and thermal robustness are combined in compounds **1**, **2b** and **3b**. The molecular structure of **1** reveals that the titanyl group creates a dome over the macrocycle. As a consequence two sets of *endo* and *exo* methyl groups are observed in ^{1}H and ^{13}C NMR spectra. Face-to-face dimer formation is hindered by this bulky ligand. To the best of our knowledge, this is the first crystal structure reported for a soluble non-aggregated titanyl phthalocyanine. Our next goals are investigations of collective optophysical properties and of the reactivity of these new titanyl phthalocyanines. Special focus will lie on physical vapour deposition experiments and the physical investigation of ordered mono- and multilayers of **1**.

Appendix A. Supplementary material

Selected NMR and UV–Vis spectra are given in the supporting information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.099.

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