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Synthesis and derivatization of near-IR absorbing titanylphthalocyanines with dimethylaminoethylsulfanyl substituents

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Abstract

Several titanium phthalocyanines tetra- and octa-substituted with dimethylaminoethylsulfanyl groups on peripheral positions have been synthesized and characterized. These phthalocyanines were converted into water-soluble quaternized products by reaction with methyl iodide. The capping of the titanyl (metaloxo) inner core with catechol and 2,3-dihydroxynaphthalene and complexation of peripheral donor groups of octakis(2-dimethylaminoethylsulfanyl)phthalocyaninatooxotitanium(IV) with Pd(II) ions to obtain multinuclear product were also studied. The new compounds were characterized using elemental analyses, ^{1}H NMR, IR, mass and UV–vis spectral data.

Keywords: Phthalocyanine; Titanyl; Water-soluble; Near-IR absorber; Axial substitution; Palladium

1. Introduction

Phthalocyanines have attracted considerable interest for many decades because of their remarkable thermal and chemical stability; they have been used as excellent dyes and pigments for many years. Current research on phthalocyanines has expanded into several applied fields including photovoltaics, electrochromism, optical data storage, laser dyes, liquid crystals, as well as chemical sensors and photosensitizers for photodynamic therapy [1,2]. The properties of phthalocyanines are influenced both by the nature of the substituents (electron donating or electron withdrawing) on the ligand and by the nature of the metal ion in the core of the ligand.

Many metallo-phthalocyanine materials with different metal atoms have been synthesized over the past few decades, such as NiPc, ZnPc, MgPc, TiOPc, VOPc, etc. In contrast to other metallo-phthalocyanines with divalent metal ions (e.g. NiPc, ZnPc), TiOPc is a nonplanar, polar molecule with the titanyl group located perpendicular to the macrocycle [3,4]. Both the nonpolarity and the dipolar character of the molecule result in a specific polymorphism that differs significantly from that of planar phthalocyanines [5]. Another motive of interest in the preparation of peripherally substituted phthalocyaninatotitanium(IV) oxide and related compounds relies upon the possibility of creating materials with remarkable nonlinear optical (NLO) properties [6–8]. In particular, titanylphthalocyanine (TiOPc) has light sensitivity shifted to the infrared region, which leads their use as photoconductive materials for printers and copying machines [9–11]. These features are stronger when compared to the other metallophthalocyanines. There has been a considerable interest in the development of the chemistry and applications of phthalocyaninatotitanium(IV) complexes in recent years [12–17]. The presence of axial ligands can change the magnitude of the intermolecular interactions in the different axially substituted titanium(IV) phthalocyanines [18] and it is also expected to produce a favourable effect on the NLO properties of the resulting molecules.

In general, unsubstituted metal-free and metallo-phthalocyanine derivatives are known to be insoluble or slightly soluble in common organic solvents, a characteristic that has proven to be the problematic in terms of their application in various

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fields. Substitution at the periphery of the macrocycle reduces the strong interaction between rings and leads to highly soluble compounds in either aqueous media or common organic solvents and also offers a useful way for tuning the wavelength of the absorption band [19–28]. A consequence of incorporating a sulfanyl function on the periphery has been the shift of Q-band absorption to longer wavelengths [29–33], which is preferred for number of applications such as IR-absorbers and photosensitizers. Quaternized ammonium groups are also useful substituents by providing solubility within a wide pH range [34,35].

In a recent work we have proved that in addition to sulfanyl moieties on the periphery when TiO^{+2} is used in the inner core, absorption maxima of the Q-band have been shifted totally to IR region [17]. In the present paper, our aim was to prepare tetra- and octa-dimethylaminoethylsulfanyl substituted phthalocyaninatooxotitanium(IV) complexes carrying sulfanyl, quaternary ammonium and titanyl functions simultaneously in order to make use of their solubilizing effect in aqueous media as well as the shift of the Q-band to the near-IR range. Capping of titanyl (metaloxo) inner core with catechol and 2,3-dihydroxynaphthalene and complexation of peripheral donor groups of octakis(2-dimethylaminoethylsulfanyl)phthalocyaninatooxotitanium(IV) with Pd(II) ions to obtain multinuclear product have been also studied.

2. Experimental

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. ^1H NMR spectra were recorded on Bruker 250 MHz spectrometer using TMS as internal reference. Mass spectra were recorded on a Varian 711 spectrometer. All reagents and solvents were of reagent grade obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [36]. The homogeneity of the products was tested in each step by TLC. The solvents were stored over molecular sieves. 4-Nitro-1,2-dicyanobenzene [37], 4,5-dichloro-1,2-dicyanobenzene [29], 4-(2-dimethylaminoethylsulfanyl)-1,2-dicyanobenzene (**1**) [38] and 4,5-bis(2-dimethylaminoethylsulfanyl)-1,2-dicyanobenzene (**2**) [39] were synthesized according to published methods.

*2.1. 2,9,16,23-Tetrakis(2-dimethylaminoethylsulfanyl)-phthalocyaninatooxotitanium(IV) (**3**) and 2,3,9,10,16,17,23,24-octakis(2-dimethylamino-ethylsulfanyl)phthalocyaninatooxotitanium(IV) (**4**)*

A mixture of appropriate ratio of 4-(2-dimethylaminoethylsulfanyl)-1,2-dicyanobenzene (**1**) (0.23 g, 1 mmol) or 4,5-bis(2-dimethylaminoethylsulfanyl)-1,2-dicyanobenzene (**2**) (0.335 g, 1 mmol) and urea (0.03 g, 0.5 mmol) was dissolved in dried *n*-pentanol (1 ml). Titanium tetraisopropylate (0.15 ml, 0.5 mmol) was added via micropipette. The reaction mixture was heated with stirring at 140 °C under nitrogen for 24 h. After cooling to room temperature, the reaction mixture of **3** was poured into water, filtered off, then washed with water several times and with cold ethanol and finally dried *in vacuo*. The dark green metallo-phthalocyanine **3** was isolated on a neutral alumina column with THF–MeOH (20:1) as eluent. After cooling to room temperature, to the reaction mixture of **4**, MeOH (20 ml) was added in order to precipitate the product. The precipitate was filtered off and washed with methanol, water and again with methanol and finally the solid washed with acetone to remove unreacted materials. Finally, a dark colored pure phthalocyanine derivative (**4**) was obtained by chromatography on silica gel column using ethyl acetate–hexane (1:1) as eluent.

*2.1.1. Compound **3***

Yield: 0.11 g (18%); mp > 200 °C; IR, ν (cm^{-1}): 2934–2765, 1597, 1455, 1387, 1319, 1060, 963; ^1H NMR ($CDCl_3$): δ 8.62–7.47 (m, 12H, Ar–H), 3.5 (t, 8H, SCH_2), 2.89 (t, 8H, NCH_2), 2.47 (s, 24H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 344 (4.56), 652 (4.25), 723 (4.87); Anal. Calcd for $C_{48}H_{52}N_{12}OS_4Ti$: C 58.28, H 5.3, N 16.99. Found: C 58.16, H 5.09, N 16.87; MS (FAB) *m/z*: 988.25 $[M]^+$, 989.16 $[M+1]^+$, 990.51 $[M+2]^+$, 572.27 $[M-(4\times SCH_2CH_2N(CH_3)_2)]$.

*2.1.2. Compound **4***

Yield: 0.27 g, (19%); mp > 200 °C; IR, ν (cm^{-1}): 2933–2763, 1589, 1456, 1368, 1316, 1061, 963; ^1H NMR ($CDCl_3$): δ 8.9 (s, 8H, H–Ar), 3.47 (t, 16H, S–CH_2), 2.9 (t, 16H, N–CH_2), 1.83 (s, 48H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 338 (4.76), 658 (4.32), 739 (4.90); Anal. Calcd for $C_{64}H_{88}N_{16}OS_8Ti$: C 54.83, H 6.33, N 15.99. Found: C 54.28, H 6.09, N 15.47; MS (FAB) *m/z*: 1401.88 $[M+1]^+$.

*2.2. 2,9,16,23-Tetrakis(2-trimethylaminoethylsulfanyl)-phthalocyaninatooxotitanium(IV) tetraiodide (**3a**) and 2,3,9,10,16,17,23,24-octakis(2-trimethylamino-ethylsulfanyl)phthalocyaninatooxotitanium(IV) octaiodide (**4a**)*

Compound **3** (0.10 g, 0.1 mmol) or **4** (0.140 g, 0.1 mmol) and methyl iodide (0.07 g, 0.5 mmol for **3**; 0.140 g, 1 mmol for **4**) were dissolved in chloroform (10 ml) and stirred at reflux temperature for 3 h. After cooling to room temperature, the mixture was filtered off and the residue was washed with methanol, chloroform and acetone successively to afford pure compounds **3a** and **4a**.

*2.2.1. Compound **3a***

Yield: 0.57 g (59%); mp > 200 °C; IR (KBr), ν (cm^{-1}): 3005–2855, 1598, 1472, 1386, 1318, 1063, 963, 905; ^1H NMR (DMSO): δ 9.61–7.78 (m, 12H, Ar–H), 4.06 (t, 8H, SCH_2), 3.88 (t, 8H, NCH_2), 3.37 (s, 24H, CH_3); UV–vis (H_2O) λ_{max}/nm (log ε): 350 (4.59), 680 (4.85); Anal. Calcd for $C_{52}H_{64}I_4N_{12}OS_4Ti$: C 40.12, H 4.14, N 10.80. Found: C 40.01, H 4.09, N 10.67; MS (FAB) *m/z*: 1556.89 $[M+1]^+$, 1047.98 $[M-I_4]$, 812.97 $[M-(I_4+4\times N(CH_3)_2)]$, 572.82 $[M-(I_4+(4\times SCH_2CH_2N(CH_3)_2))]$.

2.2.2. Compound **4a**

Yield: 0.1 g (%72); mp > 200 °C; IR, ν (cm^{-1}): 2982–2876, 1593, 1474, 1408, 1372, 1067, 963; ^1H NMR ($CDCl_3$): δ 9.25 (s, 8H, H–Ar), 3.95 (t, 16H, S–CH_2), 3.80 (t, 16H, N–CH_2), 3.25 (s, 48H, CH_3); UV–vis (DMSO) λ_{max}/nm (log ε): 378 (4.75), 648 (4.34), 722 (4.91); Anal. Calcd for $C_{72}H_{112}I_8N_{16}OS_8Ti$: C 34.08, H 4.45, N 8.83. Found: C 33.87, H 4.28, N 8.72.

2.3. Catecholato-2,9,16,23-tetrakis(2-dimethylaminoethylsulfanylphthalocyaninato) titanium(IV) (**3b**) and catecholato-2,3,9,10,16,17,23,24-octakis(2-dimethylaminoethylsulfanylphthalocyaninato) titanium(IV) (**4b**)

Compound **3** (0.1 g, 0.1 mmol) or **4** (0.140 g, 0.1 mmol) and catechol (0.011 g, 0.1 mmol) were dissolved in chloroform (20 ml) and stirred at reflux temperature for 3 h. After cooling the mixture, the solvent was removed *in vacuo*. The residue was washed with methanol and dark colored product was dried *in vacuo*. The resulting greenish black metallophthalocyanine was isolated on a silica gel column with hexane–toluene (1:9) mixture as eluent.

2.3.1. Compound **3b**

Yield: 0.084 g (78%); mp > 200 °C; IR, ν (cm^{-1}): 2935–2777, 1596, 1457, 1390, 1316, 1245, 1057, 915; ^1H NMR ($CDCl_3$): δ 8.85–7.67 (m, 12H, Ar–H), 5.25 (m, 2H, Ar–H), 4.02 (m, 2H, Ar–H), 3.64 (t, 8H, SCH_2), 3.0 (t, 8H, NCH_2), 2.53 (s, 24H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 331 (4.75), 650 (4.56), 720 (4.94). Anal. Calcd for $C_{54}H_{56}N_{12}O_2S_4Ti$: C 59.99, H 5.22, N 15.55. Found: C 59.86, H 5.09, N 15.37.

2.3.2. Compound **4b**

Yield: 0.095 g (64%); mp > 200 °C; IR, ν (cm^{-1}): 2978–2855, 1651, 1421, 1268, 1114, 834; ^1H NMR ($CDCl_3$): δ 8.9 (s, 8H, Ar–H), 5.3 (m, 2H, Ar–H), 4.13 (m, 2H, Ar–H), 3.47 (t, 16H, SCH_2), 2.9 (t, 16H, NCH_2), 2.47 (m, 48H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 328 (4.57), 658 (4.69), 729 (4.92); Anal. Calcd for $C_{70}H_{92}N_{16}O_2S_8Ti$: C 56.28, H 6.21, N 15. Found: C 56.06, H 6.09, N 14.77.

2.4. (2,3-Naphthalenediolato)-2,(3)-tetra-2-dimethylaminoethylsulfanylphthalocyaninato) titanium(IV) (**3c**) and (2,3-naphthalenediolato)-2,(3)-octa-2-dimethylaminoethylsulfanylphthalocyaninato) titanium(IV) (**4c**)

A stirred solution of compound **3** (0.1 g, 0.1 mmol) or **4** (0.14 g, 0.1 mmol) and 2,3-dihydroxynapthalene (0.032 g, 0.2 mmol) in $CHCl_3$ (20 ml) was heated for 1 h at 50 °C. After cooling to room temperature the solvent was removed under vacuum and the crude product was recrystallized from dichloromethane by addition of methanol, the pure product was dried *in vacuo*.

2.4.1. Compound **3c**

Yield: 0.035 g (60%); mp > 200 °C; IR, ν (cm^{-1}): 2935–2765, 1596, 1444, 1315, 1253, 915, 817; ^1H NMR ($CDCl_3$): δ 8.87–8.08 (m, 12H, Ar–H), 6.35 (m, 4H, Ar–H), 4.25 (s, 2H, Ar–H), 3.64 (t, 8H, SCH_2), 3.0 (t, 8H, NCH_2), 2.54 (s, 24H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 280 (4.63), 340 (4.77), 656 (4.64), 720 (4.94); Anal. Calcd for $C_{58}H_{58}N_{12}O_2S_4Ti$: C 61.58, H 5.17, N 14.86. Found: C 61.46, H 5.09, N 14.77.

2.4.2. Compound **4c**

Yield: 0.11 g (71%); mp > 200 °C; IR, ν (cm^{-1}): 2931–2767, 1590, 1475, 1371, 1257, 1061, 851; ^1H NMR ($CDCl_3$): δ 9.1 (br, 8H, Ar–H), 6.5 (m, 4H, Ar–H), 4.5 (s, 2H, Ar–H), 3.62 (t, 16H, S–CH_2), 3.0 (t, 16H, N–CH_2), 1.67 (s, 48H, CH_3); UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 280 (4.61), 334 (4.84), 656 (4.61), 741 (4.87). Anal. Calcd for $C_{74}H_{94}N_{16}O_2S_8Ti$: C 57.56, H 6.14, N 14.51. Found: C 57.46, H 6.09, N 14.37.

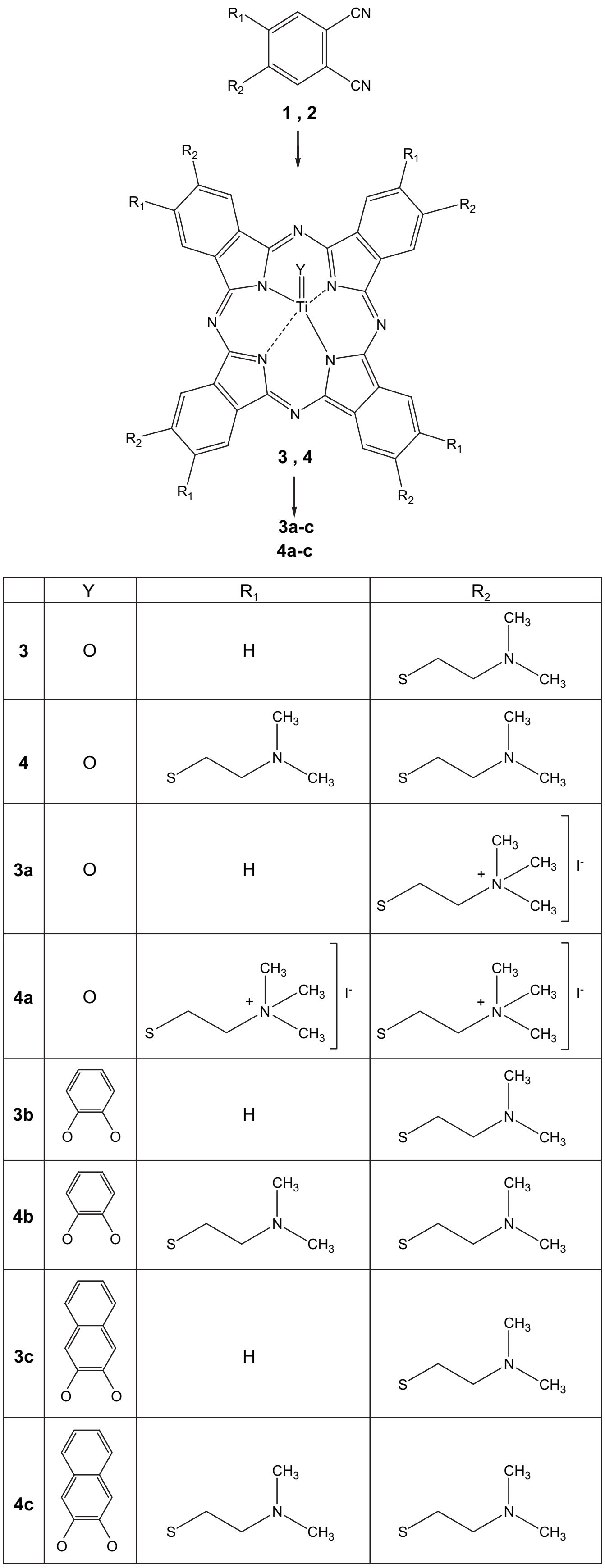
2.5. Octakis(2-dimethylaminoethylsulfanyl)-phthalocyaninatooxotitanium(IV)-tetra palladium(II) (**4d**)

Compound **4** (0.070 g, 0.05 mmol) was dissolved in THF–water (35:1) and a solution of $Na_2[PdCl_4]\cdot 3H_2O$ (0.140 g, 0.4 mmol) was added. The reaction mixture became dark green while refluxing for 3 h and precipitation occurred. The dark green product was filtered off and washed several times with hot water, hot chloroform, and finally with hot ethanol. Yield: 0.068 g (65%); mp > 200 °C; IR, ν (cm^{-1}): 2987–2926, 1617, 1457, 1406, 1065, 973, 931; UV–vis ($CHCl_3$) λ_{max}/nm (log ε): 335 (4.76), 648 (4.47), 722 (4.89). Anal. Calcd for $C_{64}H_{88}N_{16}OPd_4S_8Ti$: C 36.27, H 4.57, N 10.57. Found: C 36.18, H 4.49, N 10.47.

3. Results and discussion

The synthetic route in this work, as outlined in Scheme 1, is started with the synthesis of two phthalonitrile derivatives, namely 4-(2-dimethylaminoethylsulfanyl)phthalonitrile (**1**) and 4,5-bis(2-dimethylaminoethylsulfanyl)phthalonitrile (**2**) [38,39]. Treatment of **1** and **2** with titanium(IV) tetraisopropylate and urea in *n*-pentanol afforded tetrakis(2-dimethylamino ethylsulfanylphthalocyaninato)oxotitanium(IV) (**3**) and octakis(2-dimethylaminoethylsulfanylphthalocyaninato)oxotitanium(IV) (**4**), respectively. Characterization of the products involved a combination of methods including elemental analysis, ^1H NMR, FT-IR, UV–vis and Mass spectroscopy. Spectral investigations for all new products are consistent with the assigned formulations.

In the IR spectrum of **1** and **2**, stretching vibrations of C≡N groups appeared as a single intense peak at expected frequencies [40–42]. These peaks disappeared after conversion into phthalocyanines **3** and **4** in the next step. The presence of an oxo group in these compounds was revealed by the medium band at about 960 cm^{-1} in their IR spectra



Scheme 1.

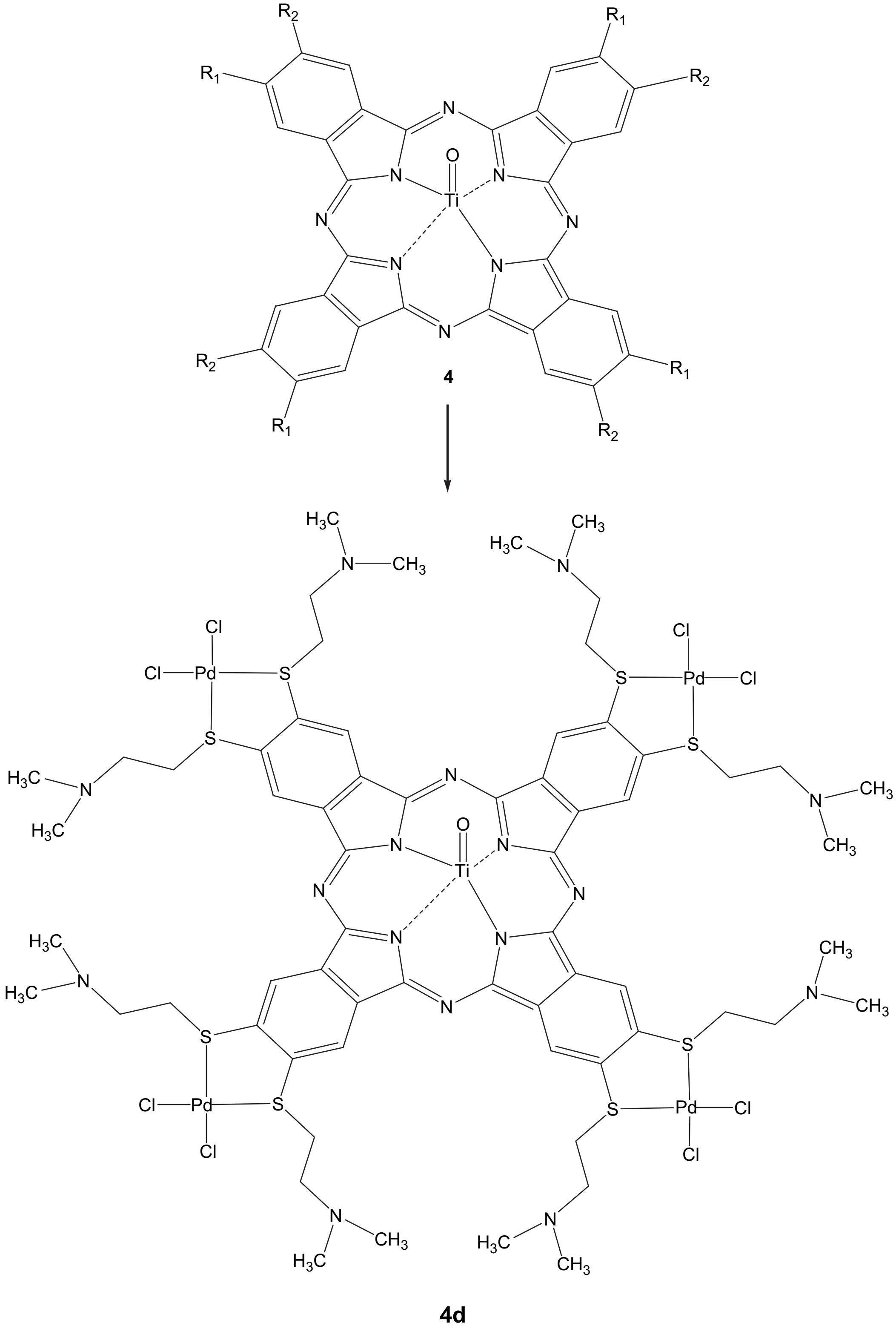
assignable to the Ti═O stretch. The ^{1}H NMR spectra were in accord with the proposed structures. The ^{1}H NMR data of **3** (or **4**) showed chemical shifts assignable to Ar–H, S–CH_2, N–CH_2 and CH_3 protons at 8.62–7.47 (8.9), 3.5 (3.47), 2.89 (2.9) and 2.47 (1.83) ppm, respectively.

Reported examples of water-soluble phthalocyanine derivatives possess sulfo-, amino-, carboxy-, or phosphoro-substituents which are used in compounds that have been synthesized for a new generation of photosensitizers [43,44]. Peripheral dimethylaminoethyl substituents of titanylphthalocyanines **3** and **4** are extremely suitable for conversion into quaternary ammonium groups which lead to products soluble in aqueous media. When phthalocyanines were treated with methyl iodide in chloroform, hydrophilic phthalocyanine products **3a** and **4a** with four or eight quaternary ammonium groups were obtained [34,35,45,46]. No major changes in the IR spectra were found after quaternization. When compared to the high solubility of quaternized phthalocyanines in aqueous solutions, **3a** has a better solubility especially in water than **4a**.

We have also prepared the axially substituted titanium(IV) phthalocyanines **3b**, **4b**, **3c**, **4c** starting from **3** and **4** using catechol and 2,3-dihydroxynaphthalene as axial ligands. For the synthesis of axially substituted titanium(IV) phthalocyanines, chelating agents with two hydroxyl groups were heated with **3** and **4** in chloroform and purified first by washing with methanol to remove the remaining catechols or 2,3-dihydroxynaphthalene and finally isolated by column chromatography. The absence of the Ti═O band around 960 cm^{-1} in the IR spectra of products (**3b**, **4b**, **3c**, **4c**) reveals the complete reaction of phthalocyaninatotitanium oxide with the ligands. In the ^{1}H NMR spectra, the protons of the axial ligand, in general give upfield-shifted signals due to the phthalocyanine ring-current effect [6,47,48]. These signals are found for **3b** (or **4b**) at around 5.25 and 4.02 (or 5.3 and 4.13) ppm assignable to the two sets of protons of the catecholato group and for **3c** (or **4c**) at 6.35 and 4.85 (or 6.5 and 4.9) ppm of protons of the naphthalenediolato group.

Phthalocyanines with S-donor groups on the periphery have been shown to be capable of binding transition metal ions [31,46]. The interaction of the palladium(II) ion with the thioether groups of the phthalocyanine (**4**) gave a product (**4d**) with a phthalocyanine–metal ratio of 1:4 (Scheme 2). It can be easily differentiated from the precursor **4** by its different green tone. The solubility of this pentanuclear product is lower than the corresponding titanium phthalocyanine (**4**). In the case of complexes of phthalocyaninatotitanium(IV) oxide with Pd(II), ^{1}H NMR spectra are further broadened and the aromatic protons are hardly detectable.

The phthalocyanines show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B-band) and the other in the visible portion at 600–700 nm (Q-Band). These absorptions can be shifted to near-IR by making relatively small changes on phthalocyanines such as addition of aromatic rings or electron donating groups into the periphery of phthalocyanines or using of some metal ions in the inner core. The characteristic Q-band absorption maxima of similar phthalocyanines with



4

4d

Scheme 2.

divalent Zn ion at the inner core are at 685 nm for tetrakis(dimethylaminoethylsulfanyl) substituted phthalocyanine and at 715 nm for octakis-substituted analog. The presence of TiO^{+2} moieties in the inner core of these products shifted their absorptions to the near-IR region. UV–vis spectra of phthalocyanines **3** and **4** exhibited the intense Q-band absorption of the $\pi-\pi^*$ transitions at 723 and 739 nm (listed in Table 1). When these products are quaternized, the influence of the solvent polarity on the absorption maxima can be clearly verified by maximum absorption for **3a** in water at

Table 1
Electronic spectra of phthalocyanines

Compound	λ_{max}/nm (log ε)			
3[a]	723 (4.87)	652 (4.25)	344 (4.56)	
4[a]	739 (4.90)	658 (4.32)	338 (4.76)	
3a[b]	680 (4.85)		350 (4.59)	
4a[c]	722 (4.91)	648 (4.34)	378 (4.75)	
3b[a]	720 (4.94)	650 (4.56)	331 (4.75)	
4b[a]	729 (4.92)	658 (4.69)	328 (4.57)	
3c[a]	720 (4.94)	656 (4.64)	340 (4.77)	280 (4.63)
4c[a]	741 (4.87)	656 (4.61)	334 (4.84)	280 (4.61)
4d[a]	722 (4.89)	648 (4.47)	335 (4.76)	

[a] In $CHCl_3$.
[b] In water.
[c] In DMSO.

680 nm and for **4a** in DMSO at 722 nm. Capping of TiO moiety with catechol or 2,3-naphthalenediol groups does not cause appreciable change in lower energy absorption maxima if the measurements are carried out in the same organic solvents.

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