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Near-IR absorbing phthalocyanines

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Abstract

Phthalocyanines with four or eight hexylthio-substituents on the periphery were prepared by cyclotetramerization of 4-hexylthio-1,2-dicyanobenzene and 4,5-bis(hexylthio)-1,2-dicyanobenzene. The new compounds were characterized by elemental analyses, ^{1}H NMR, IR and UV–VIS spectral data. The electronic spectra exhibit intense Q band near-IR region at 720 nm for the tetrahexylthio-substituted phthalocyanine and at 739 nm for the octa-substituted one together with less intense B band near UV range.

Keywords: Phthalocyanine; Titanyl; Near-IR absorber; Pyrocatechol

1. Introduction

An important challenge in creating molecules with desired optical properties lies in achieving a well-defined architecture while maintaining adequate electron density throughout the whole molecule [1]. Organic materials with intense absorptions in the near-IR region (i.e. 750–1300 nm) are particularly important in number of applications including thermal imaging, optical data storage, automatic identification, etc. [2]. Phthalocyanines with highly delocalized cyclic π-electron systems show intense absorptions in the red region (Q band) and these absorptions can be shifted to near-IR by making relatively small changes on these molecules [3,4]. Fusion of additional aromatic rings (polybenzannulation) has been proposed as a practical method to enhance the conjugation of π-electrons and so increasing the wavelength of absorbed electromagnetic radiation, but the insolubility of the products obtained here has been almost inevitable [5]. The second way to obtain the same effect has been the addition of electron donating groups (e.g. −OR, −SR, etc.) into the periphery of the phthalocyanines [6]. The last method to change the absorbed wavelength is the use of some special metal ions in the inner core, and TiO^{+2} is one of them [7]. PcTiO derivatives are well known near-IR active photoconductive materials used as xerographic photoreceptors in copiers and laser printers [8–10]. Also this material can be used in optical disc information recording. The high third order optical susceptibility values of PcTiO derivatives have been well documented [11]. The change of axial oxo ligand with catechol derivatives has been reported as an easy procedure and a phthalocyanine pentamer consisting of mutually orthogonal phthalocyanine units has been prepared by a one step reaction [12,13]. During the preparation of this paper, Torres et al. [14] demonstrated the use of PcTiO derivative with *t*-butyl substituents on peripheral positions anchored to TiO_2 films in efficient photocurrent generation in dye sensitized photoelectrochemical solar cells.

Our research group has been intensely engaged in the development of tetrapyrrole systems that exhibit a number of functionalities such as alkali or transition metal

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binding, supramolecule formation or enhanced electrical conductance [15–20]. Because unsubstituted transition metal and metal-free phthalocyanines are insoluble in common organic solvents, the synthesis of new phthalocyanine systems has been essentially designed in such a way so that the final phthalocyanine derivatives are sufficiently soluble to perform the desired activities [21,22]. Peripheral substitution pattern has been of upper most importance in this sense and we have employed fused macrocycles, long alkoxy or alkylthio-chains in our earlier works [15–18,21–24].

In the present paper, our aim has been to prove for the first time the stepwise shift of Q band absorption in titanyl phthalocyanines to longer wavelengths by peripheral substitutions of each benzo unit with single or double alkylthio-groups. Capping of titanyl (metaloxo) inner core with 1,2-dihydroxybenzene has been also studied.

2. Experimental

IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. 4-Nitro-phthalonitrile [25], 4,5-dichloro-phthalonitrile [26], 4-hexylthio-1,2-dicyanobenzene [27] (**1**) and 4,5-bis(hexylthio)-1,2-dicyanobenzene [28] (**2**) were prepared as given in the literature.

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

A mixture of 4-hexylthio-1,2-dicyanobenzene (**1**) (0.24 g, 1 mmol) or 4,5-bis (hexylthio)-1,2-dicyanobenzene (**2**) (0.36 g, 1 mmol) and urea (0.03 g, 0.5 mmol) was dissolved in *n*-pentanol (1 ml). Then titanium tetraisopropylate (0.1472 ml, 0.5 mmol) was added via a micropipette. The reaction mixture was heated with stirring at 150 °C under nitrogen for 24 h. After cooling the mixture to room temperature, it was treated with methanol (20 ml) and the mixture was filtered off. The residue was washed with methanol (15 ml), water (20 ml) and methanol (10 ml) again and finally the solid was washed with acetone to remove unreacted materials. The resulting dark colored product was isolated on a silica gel column using ethyl acetate–hexane (1:1) as eluent.

Compound **3**: Yield 0.062 g (24%); Calcd. for $C_{56}H_{64}N_8S_4OTi$: C, 64.61; H, 6.15; N, 10.76%. Found: C, 64.34; H, 6.56; N, 10.09%. IR (KBr) ν_{max} (cm^{-1}): 2950–2870, 1600, 1510, 1470, 1410, 1350, 1090, 985, 825, 750; ^{1}H NMR ($CDCl_3$) δ: 8.62–7.01 (m, 12H), 3.33 (t, 8H), 1.96 (qnt,8H), 1.68–1.49 (m, 24H), 1.02 (t, 12H); UV–VIS ($CHCl_3$) λ_{max}(log ε) (nm): 349 (4.86), 720 (5.34).

Compound **4**: Yield 0.145 g (38%); Calcd. for $C_{80}H_{112}N_8S_8OTi$: C, 63.83; H, 7.44; N, 7.44%. Found: C, 63.34; H, 7.76; N, 7.19%; IR (KBr) ν_{max} (cm^{-1}): 2955–2870, 1605, 1510, 1470, 1410, 1095, 825, 750; ^{1}H NMR ($CDCl_3$): 8.60 (s, 8H), 3.40 (t, 16H), 1.99 (qnt, 16H), 1.70–1.44 (m, 48H), 0.97 (t, 24H); UV–VIS ($CHCl_3$) λ_{max} (log ε) (nm): 336 (5.00), 739 (5.35).

*2.2. Catecholato-2,9,16,23-tetrakis(hexylthio) phthalocyaninatotitanium(IV) (**5**) and catecholato- 2,3,9,10,16,17,23,24-octakis (hexylthio)phthalocyaninato titanium(IV) **(6)***

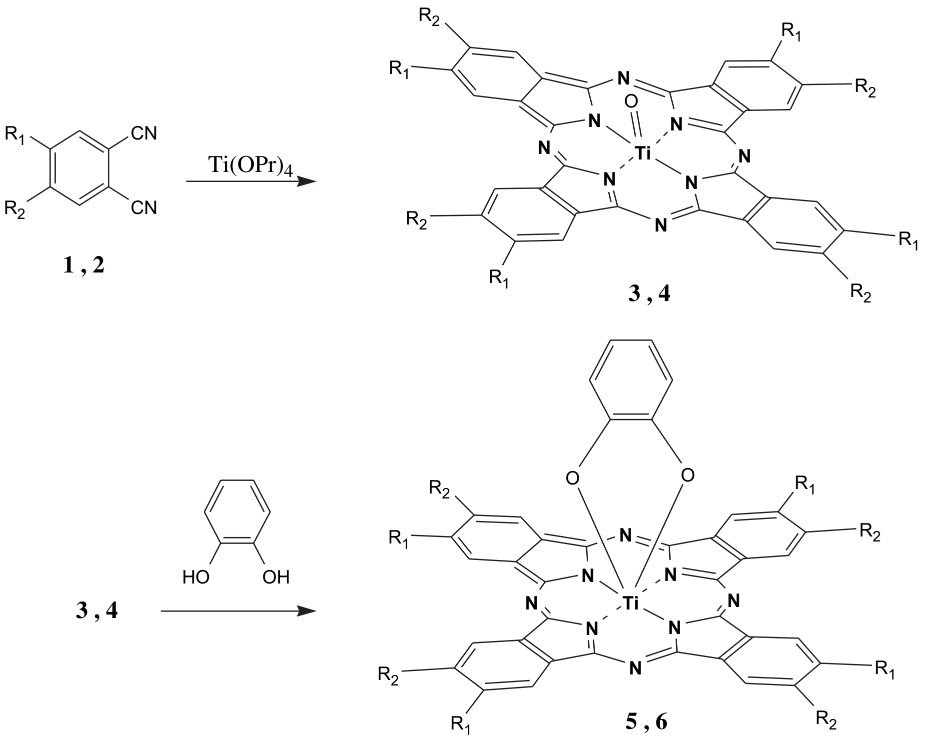
Compound **3** (0.1 g, 0.1 mmol) or compound **4** (0.15 g, 0.1 mmol) and catechol (0.011 g, 0.1 mmol) were dissolved in $CHCl_3$ (20 ml) and heated for 1 h under reflux. After cooling the mixture, the solvent was removed in vacuo. The residue was washed with methanol and dark colored product was dried in vacuo. The resulting greenish black metallophthalocyanine was isolated on a silica gel column with hexane–toluene (1:9) as eluent.

Compound **5**: Yield 0.070 g (64%); Calcd. for $C_{62}H_{68}N_8S_4O_2Ti$: C, 65.72; H, 6.00; N, 9.88%. Found: C, 66.10; H, 6.35; N, 9.72%; IR (KBr) ν_{max} (cm^{-1}): 2980–2895, 1620, 1525, 1480, 1080, 965; ^{1}H NMR: 8.42–7.21 (m, 12H), 5.34 (m, 2H), 4.20 (m, 2H), 3.21 (t, 8H), 2.15 (qnt, 8H), 1.84–1.41 (m, 24H), 1.09 (t, 12H); UV–VIS ($CHCl_3$) λ_{max} (log ε) (nm): 342 (4.64), 721 (5.12).

Compound **6**: Yield 0.095 g (59%); Calcd. for $C_{62}H_{68}N_8S_4O_2Ti$: C, 64.66; H, 7.26; N, 7.01%. Found: C, 64.10; H, 7.45; N, 7.72%; IR (KBr) ν_{max} (cm^{-1}): 2980–2890, 1620, 1530, 1480, 1080; ^{1}H NMR ($CHCl_3$): 8.65 (s, 8H), 5.35 (br s, 2H), 4.18 (br s, 2H), 3.42 (t, 16H), 1.99 (qnt, 16H), 1.68–1.44 (m, 48H), 0.95 (t, 24H); UV–VIS ($CHCl_3$) λ_{max} (log ε) (nm): 335 (5.07), 741 (5.36).

3. Results and discussion

The synthetic procedure, as outlined in Scheme 1, started with the synthesis of two phthalonitrile derivatives, namely 4-hexylthio-1,2-dicyanobenzene (**1**) and 4,5-bis(hexylthio)-1,2-dicyanobenzene (**2**) [27,28]. Displacement of the nitro group in 4-nitrophthalonitrile and both of the Cl moieties in 4,5-dichlorophthalonitrile with hexanethiol in the presence of anhydrous K_2CO_3 in DMF at room temperature gave the desired phthalonitrile derivatives **1** and **2**, respectively. Treatment of either of these two precursors with titanium(IV) isopropoxide



	1, 3, 5	2, 4, 6
R_1	H	$C_6H_{13}S$
R_2	$C_6H_{13}S$	$C_6H_{13}S$

Scheme 1.

and urea in pentanol lead to the corresponding metallophthalocyanines **3** and **4**, respectively [9]. A noteworthy observation during the synthesis was the dark color of the product especially for the latter in contrast to the usual dark green or dark blue color frequently encountered. Capping of TiO core of **3** or **4** with catechol was accomplished by treatment of the oxo complex with catechol in refluxing chloroform [9,12,13].

All phthalocyanines **3–6** are soluble in a number of solvents such as chloroform, dichloromethane, THF, etc. Elemental analysis and spectral data (^{1}H NMR, FT-IR, UV–VIS) for all new products are consistent with the assigned formulations. In mono- (**1**) and di-substituted phthalonitriles (**2**), stretching vibrations of C≡N groups appeared as a single intense peak at expected frequencies [15–17]. These peaks disappeared after conversion into phthalocyanines **3** and **4**. A typical absorption around 960 cm^{-1} in products **3** and **4** can be easily assigned to Ti=O stretching [9]. Capping of these oxo complexes with catechol to form **5** and **6** was confirmed by the disappearance of the characteristic absorptions around 960 cm^{-1}.

^{1}H NMR spectra of the phthalonitriles (**1**, **2**) and titanyl phthalocyanines (**3**, **4**) are almost identical. However, capping with catechol brings out totally new chemical shifts. In the ^{1}H NMR spectra of **5** and **6** two broad signals around 5.25 and 4.18 ppm assignable to the two sets of protons of the catecholato group are shifted up field by the phthalocyanine ring current [12].

The electronic spectra of the titanyl phthalocyanines **3** and **4** are especially noteworthy (Fig. 1). Q band absorption maxima of similar phthalocyanines with divalent Ni ion at the inner core are at 687 nm for tetra-(alkylthio) substituted phthalocyanine and at 702 nm for octa-substituted analog. Insertion of TiO^{+2} moieties into these products shifted their absorptions to 720 nm in **3** and 739 nm in **4**. The consequence of this bathochromic shift is a black colour especially for the latter in contrast to the usual dark blue or dark green colour of phthalocyanine derivatives. The absorption maxima of catechol capped phthalocyanines **5** and **6** do not show appreciable change when compared with the titanyl derivatives **3** and **4** and such a result is expected from the similar experimental data reported.

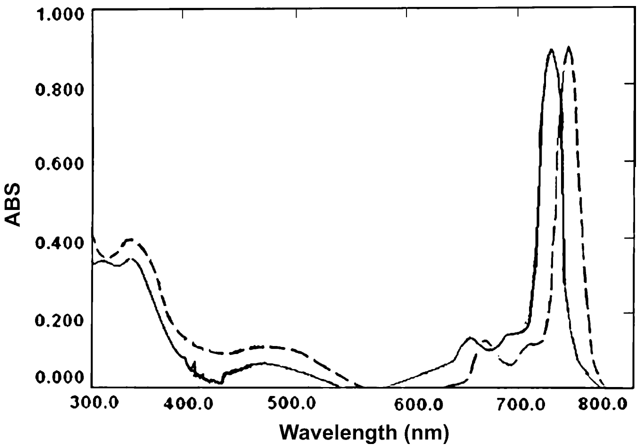


Fig. 1. Electronic spectra of **3** (——) and **4** (- - -).

In conclusion, substitution of phthalocyanine cores with sulfur donors and insertion of titanyl moieties into the inner core simultaneously result with products absorbing in the longer wavelengths. Carrying out these two bathochromic shift procedures simultaneously on the same phthalocyanine core enables us to reach products absorbing in near-IR range.

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