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Received August 20, 1996  
Revised October 3, 1996

Three novel unsymmetrical vanadyl dodecakis(2,2,2-trifluoroethoxy)phthalocyaninates with nitro, amino or with no substitution were synthesized by a statistical condensation of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile with 4-nitro, 4-amino or 4-unsubstituted phthalonitrile, and separated by common column chromatography. These highly soluble phthalocyanines were characterized by elemental analysis, ir and  $^1\text{H}$ -nmr, uv-visible and fast-atom-bombardment mass spectroscopy. Their uv-visible absorption spectra in solution and in doped poly(methyl methacrylate) films showed that they were less aggregated unsymmetrical phthalocyanines.

*J. Heterocyclic Chem.*, **34**, 171 (1997).

### Introduction.

For many years, phthalocyanines have continuously attracted great interests in various research fields such as chemical sensors, electrochromism, batteries, semiconductors, molecular metals, catalysts, photochemical hole burning, liquid crystals and nonlinear optics [1-3]. Although a variety of symmetrical or pseudosymmetrical tetra-, octa- and hexadecasubstituted phthalocyanines [1-3] have been reported in the literatures up to now, there have been few reports on unsymmetrically substituted phthalocyanines, mainly because of their preparative difficulties. Unsymmetrical phthalocyanines are expected to show interesting properties in the areas like liquid crystals [4], second-order nonlinear optics [5], photodynamic therapy [6] and Langmuir-Blodgett film formation [7], and can be used as intermediates for the synthesis of polymeric phthalocyanines [4b,8]. They are also very important in understanding the nature of phthalocyanines.

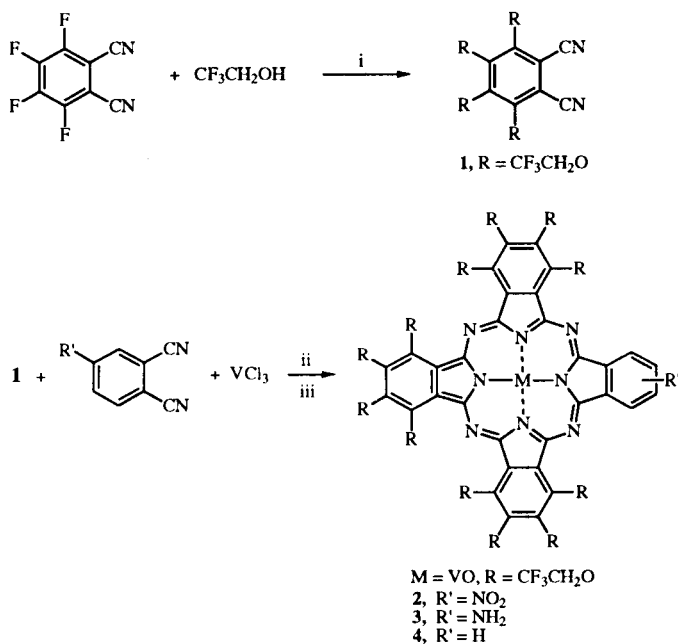
Generally speaking, unsymmetrical phthalocyanines can be prepared by several strategies: the polymer support route [9], the subphthalocyanine route [10], and the statistical condensation route [11]. The polymer support route makes the separation of unsymmetrical phthalocyanines possible and comparatively easy, however, it usually takes more steps, so this method is rather complicated. The subphthalocyanine route has been considered to be the most efficient way of obtaining unsymmetrical phthalocyanines with identical substituents on three of the benzene units and a different substituent on the fourth one, however, its overall yield is not so satisfactory. Besides, this route is not suitable for the preparation of alkoxy-substituted phthalocyanines, as this method uses boron tribromide, an ether-cleaving reagent. The statistical condensation route is the most common method to synthesize unsymmetrical phthalocyanines. Nevertheless, the mixed condensation of two differently substituted phthalonitriles or corresponding 1,3-diiminoisindolines usually gives statistical mixtures of six constitutional isomers that can not be easily separated

by chromatographic methods. Recently, a procedure which reduces the number of possible phthalocyanine isomers by using a phthalonitrile bearing in 3,6-positions sterically crowded groups such as phenyl as starting material has been reported [12]. On the other hand, if two different phthalonitriles with quite different solubility can be condensed by the statistical condensation method, the separation of unsymmetrical phthalocyanines may become possible and easy, due to the different solubility of the resulting different phthalocyanines.

In order to search for new second-order nonlinear optical materials, we are interested in unsymmetrical phthalocyanines with donors and acceptors. Previously we have reported the synthesis and second-order nonlinear optical properties of a novel unsymmetrical phthalocyanine with a nitro group as an acceptor substituent and three *tert*-butyl groups as donor groups [5b,5c,11h]. Recently, we succeeded in the preparation of new unsymmetrically dodecakis(trifluoroethoxy)-substituted vanadylphthalocyanines which have a different substituent like a nitro or an amino group or the comparable position unsubstituted on one of the benzene units (see Scheme 1). There are several reasons why we designed and synthesized such unsymmetrical phthalocyanines. First, we introduced twelve trifluoroethoxy groups on three of the benzene units in order to enhance the solubility and suppress the intermolecular aggregation effect of the target phthalocyanines, because the molecular aggregation has an important influence on the linear and nonlinear optical properties of metallophthalocyanine films [13]. Secondly, we selected vanadyl as the central metal part, because in our previous research we found out the vanadyl phthalocyanine films have large third harmonic susceptibilities  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  among different metallophthalocyanine films [14]. Moreover, twelve trifluoroethoxy groups can also serve as donor groups stronger than *tert*-butyl groups, thus the target unsymmetrical phthalocyanines are not only third order nonlinear optical materials but also can be expected to have

second-order nonlinear optical properties because of their unsymmetrical structures. Finally, the target unsymmetrical phthalocyanines can be expected to have high thermal stability. In this paper, the synthesis, characterization and aggregation properties of these novel unsymmetrical phthalocyanines are reported.

Scheme 1



Reagents and conditions: i, potassium carbonate/*N,N*-dimethylformamide, room temperature, 12 hours; ii, urea, 180-200°, 2-5 hours; iii, H<sup>+</sup>/water, reflux, 2-6 hours.

## EXPERIMENTAL

The ir spectra were recorded on a Shimadzu FTIR-4100 Fourier transform infrared spectrophotometer, using potassium bromide pellets of solid. The <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectra with tetramethylsilane as the internal standard were recorded on a JEOL JNM-EX270 Fourier transform nuclear magnetic resonance spectrometer (270 MHz). Electron ionization mass spectra were recorded on a Hitachi M-80A mass spectrometer. Fast-atom-bombardment mass spectra with *m*-nitrobenzyl alcohol as a matrix were recorded on a JEOL JMS-HX110 mass spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory of our institute. The uv-visible absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer in a quartz cell of path length 10 mm. Column chromatography was performed using silica gel of particle size 63-200 μm which was produced by Merck Company. 3,4,5,6-Tetrafluorophthalonitrile (98%), 4-nitrophthalonitrile (98%), 4-aminophthalonitrile (98%) and phthalonitrile (95%) were purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. The films of poly(methyl methacrylate) doped with various concentrations of compound 2 or 3 were prepared by spin coating on indium-tin-oxide glass substrates. Typical weight concentration ranges from 0.1 to 10%.

### 3,4,5,6-Tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (1).

To a stirred solution of 3,4,5,6-tetrafluorophthalonitrile (5.70 g, 28.5 mmoles) in 2,2,2-trifluoroethanol (30.0 g, 300 mmoles) and *N,N*-dimethylformamide (50 ml), was added anhydrous potassium carbonate (20.0 g, 145 mmoles). The resulting mixture was exothermic for half an hour, and then was stirred at room temperature for 12 hours. The tlc analysis showed the disappearance of the starting material. Then 200 ml of water and 300 ml of diethyl ether were added to the resulting product mixture, and the solution was stirred for 10 minutes. The organic layer was separated and the aqueous layer was extracted with ether (3 x 50 ml). The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent to give a pale-yellow solid, which was recrystallized from methanol to yield white needle crystals of 1, 14.0 g (94%), mp 131-132°; ir:  $\nu_{\max}$  2965 (CH<sub>2</sub>), 2236 (CN), 1636, 1628 and 1574 (C=C ring), 1466 and 1456 (CH<sub>2</sub>), 1283 (C-O), 1175 (C-F), 1071, 1059, 1011 and 955 (C-O), 854 (CH<sub>2</sub>) cm<sup>-1</sup>; <sup>1</sup>H nmr (dimethyl sulfoxide-*d*<sub>6</sub>): δ 4.92 (q, J = 8.58 Hz, 4H, 3,6-(OCH<sub>2</sub>)<sub>2</sub>), 4.93 (q, J = 8.58 Hz, 4H, 4,5-(OCH<sub>2</sub>)<sub>2</sub>); <sup>13</sup>C nmr (dimethyl sulfoxide-*d*<sub>6</sub>): δ 150.7 (s, 3,6-(C<sub>aromatic</sub>)<sub>2</sub>), 148.6 (s, 4,5-(C<sub>aromatic</sub>)<sub>2</sub>), 123.2 (q, J = 278.3 Hz, CF<sub>3</sub>), 111.8 (s, CN), 105.0 (s, 1,2-(C<sub>aromatic</sub>-CN)<sub>2</sub>), 70.0 (q, J = 35.4 Hz, 3,6-(OCH<sub>2</sub>)<sub>2</sub>), 69.7 (q, J = 35.4 Hz, 4,5-(OCH<sub>2</sub>)<sub>2</sub>); ms: electron ionization m/z 520 (M<sup>+</sup>, 100), 437 (M<sup>+</sup> - CF<sub>3</sub>CH<sub>2</sub>, 68.9).

Anal. Calcd. for C<sub>16</sub>H<sub>8</sub>N<sub>2</sub>F<sub>12</sub>O<sub>4</sub> (520.23): C, 36.94; H, 1.55; N, 5.38; F, 43.82. Found: C, 37.00; H, 1.51; N, 5.38; F, 44.12.

### Vanadyl 23-Nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (2).

In a 300-ml round-bottomed three-neck flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirring bar, was placed a mixture of 3,4,5,6-tetra(2,2,2-trifluoroethoxy)phthalonitrile (3.12 g, 6.0 mmoles), 4-nitrophthalonitrile (5.19 g, 30 mmoles), vanadium trichloride (3.60 g, 22.9 mmoles) and dry urea (45 g). The mixture was stirred and heated under dry nitrogen gas. At about 150°, the mixture melted to form a liquid mixture. On further heating at a temperature of 190-200° for 5.0 hours, a black-green solid was formed. The reaction mixture was then cooled to room temperature. After the addition of 10% aqueous hydrochloric acid (180 ml), the resulting mixture was refluxed for 6 hours, and then cooled to room temperature, and neutralized with 5% aqueous sodium hydroxide solution. The black-green precipitate was filtered and washed with water, air dried. Then the crude product was dissolved in ethyl acetate, and the solution was filtered to remove the insoluble precipitate. The filtrate was condensed and the resulting residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent to give the first fraction of symmetrically hexadeca(2,2,2-trifluoroethoxy)-substituted vanadylphthalocyaninate, and the second fraction of 2. The crude unsymmetrical product was further purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent (twice) to give a dark green solid. Recrystallization from ethyl acetate-hexane (1:18, three times) yielded a dark green microcrystalline solid, 588 mg (16%); ir:  $\nu_{\max}$  3010 (=CH), 2905 (CH<sub>2</sub>), 1636, 1620 (C=C ring), 1516 (NO<sub>2</sub>), 1495 (C=C ring), 1456, 1429 (CH<sub>2</sub>), 1339 (NO<sub>2</sub>), 1275, 1246 (C-O), 1159

(C-F), 1111 (ring), 1065, 1013, 972 (C-O), 856 (CH<sub>2</sub>), 834, 764 cm<sup>-1</sup>; <sup>1</sup>H nmr (acetone-d<sub>6</sub>): δ 5.28 (m, 18H, OCH<sub>2</sub>), 5.50-6.50 (br m, 6H, OCH<sub>2</sub>), 9.33-9.75 (br, H<sub>arom</sub>); ms: fast-atom-bombardment m/z 1800.9 (M<sup>+</sup>, 100), 1718.0 (M<sup>+</sup>-CF<sub>3</sub>CH<sub>2</sub>, 25.4); uv/visible (1,4-dioxane): λ<sub>max</sub>/nm [log ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>] 730.0 (5.23), 655.5 (4.58), 347.0 (4.76), 267.0 (4.52), 234.0 (4.73).

*Anal.* Calcd. for C<sub>56</sub>H<sub>27</sub>N<sub>9</sub>F<sub>36</sub>O<sub>15</sub>V (1800.77): C, 37.35; H, 1.51; N, 7.00; F, 37.98. Found: C, 37.45; H, 1.49; N, 7.01; F, 37.79.

Vanadyl 23-Amino-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (3).

To a mixture of 3,4,5,6-tetra(2,2,2-trifluoroethoxy)phthalonitrile (3.12 g, 6.0 mmoles), 4-aminophthalonitrile (6.15 g, 42.1 mmoles) and vanadium trichloride (3.50 g, 22.3 mmoles), was added dry urea (50 g). The resulting mixture was heated at 135° for 40 minutes in an atmosphere of dry nitrogen gas, and then heated to 180°, stirred at 180-190° for 1 hour, and then at a temperature of 190-200° for 2 hours. A dark black-green solid was formed in the process of heating. The reaction mixture was then cooled to room temperature, and refluxed with 300 ml of water for 2 hours, and then cooled to room temperature. The resulting black-green precipitate was filtered and washed with water, then air-dried. The crude product was dissolved in ethyl acetate, and the solution was filtered to remove the insoluble precipitate, which was washed with ethyl acetate. The filtrate was condensed and the resulting residue was purified by column chromatography on silica gel using a 10-cm-diameter column and 3:1 (volume ratio) hexane/ethyl acetate as an eluent to give the first fraction of symmetrically hexadeca(2,2,2-trifluoroethoxy)-substituted vanadyl phthalocyaninate and the second fraction consisting largely of 3. The unsymmetrical fraction was further purified by column chromatography on silica gel with hexane/ethyl acetate (volume ratio 3:1, three times) as an eluent to give a dark purple solid. Recrystallization from ethyl acetate-hexane (1:40, twice) yielded a dark purple microcrystalline solid, 130 mg (3.7%); ir: ν<sub>max</sub> 3434 (NH), 2910 (CH<sub>2</sub>), 1636, 1626, 1489 (C=C ring), 1455, 1426 (CH<sub>2</sub>), 1277, 1246 (C-O), 1159 (C-F), 1126 (ring), 1067, 1010, 972 (C-O), 854 (CH<sub>2</sub>), 833, 760 cm<sup>-1</sup>; <sup>1</sup>H nmr (chloroform-d): δ 4.55 (m, NH<sub>2</sub>), 5.00 (m, 18H, OCH<sub>2</sub>), 5.30-6.30 (br m, 6H, OCH<sub>2</sub>), 7.70-8.30 (m, H<sub>arom</sub>); ms: fast-atom-bombardment m/z 1771.1 (M<sup>+</sup>, 100), 1688.1 (M<sup>+</sup>-CF<sub>3</sub>CH<sub>2</sub>, 20.9), 1605.1 (M<sup>+</sup>-2 x CF<sub>3</sub>CH<sub>2</sub>, 5.5); uv/visible (1,4-dioxane): λ<sub>max</sub>/nm [log ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>] 739.0 (5.08), 667.5 (4.52), 544.0 (4.10), 471.0 (3.90), 354.0 (4.80), 270.0 (4.41), 233.0 (4.67).

*Anal.* Calcd. for C<sub>56</sub>H<sub>29</sub>N<sub>9</sub>F<sub>36</sub>O<sub>13</sub>V (1770.78): C, 37.98; H, 1.65; N, 7.12; F, 38.62. Found: C, 37.95; H, 1.61; N, 6.89; F, 39.21.

Vanadyl 1,2,3,4,8,9,10,11,15,16,17,18-Dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (4).

To a mixture of 3,4,5,6-tetra(2,2,2-trifluoroethoxy)phthalonitrile (520 mg, 1.0 mmole) and phthalonitrile (680 mg, 5 mmoles), under dry nitrogen gas, were added vanadium trichloride (500 mg, 3.2 mmoles) and dry urea (7.0 g). The resulting mixture was heated at 110° for 2 hours in an atmosphere of dry nitrogen gas, and then heated to 180°, stirred at 180-185° for 2 hours. A dark blue solid was formed in the process of heating. The reaction mixture was then cooled to room temperature, and refluxed with 50 ml of 5% aqueous hydrochloric acid for 2 hours and then

cooled to room temperature. The resulting dark blue precipitate was filtered and washed with water, then air-dried. The crude product was dissolved in ethyl acetate, and the solution was filtered to remove the insoluble precipitate, which was washed with ethyl acetate until the filtrate became clear. The combined filtrates were condensed and the resulting dark-green residue was purified by column chromatography on silica gel using 3:1 (volume ratio) hexane/ethyl acetate as an eluent. The first green fraction was collected, condensed and then further purified by column chromatography on silica gel with hexane/ethyl acetate (volume ratio 3:1, twice) as eluent to give a solid which was checked by mass spectroscopy to be 4. Recrystallization from ethyl acetate-hexane (1:50) yielded a green solid, 60 mg (10%); ir: ν<sub>max</sub> 3027 (=C-H), 2905 (CH<sub>2</sub>), 1636, 1624, 1487 (C=C ring), 1456, 1431 (CH<sub>2</sub>), 1329, 1277, 1248 (C-O), 1172, 1157 (C-F), 1127 (ring), 1069, 1011, 972 (C-O), 855 (CH<sub>2</sub>), 833, 760 cm<sup>-1</sup>; <sup>1</sup>H nmr (acetone-d<sub>6</sub>): δ 5.27 (m, 18H, OCH<sub>2</sub>), 5.50-6.50 (br m, 6H, OCH<sub>2</sub>), 7.50-9.50 (br, H<sub>arom</sub>); ms: fast-atom-bombardment m/z 1756.0 (M<sup>+</sup>, 100), 1673.0 (M<sup>+</sup>-CF<sub>3</sub>CH<sub>2</sub>, 35.1), 1589.8 (M<sup>+</sup>-2xCF<sub>3</sub>CH<sub>2</sub>, 12.1); uv/visible (1,4-dioxane): λ<sub>max</sub>/nm [log ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>] 729.0 (5.22), 653.5 (4.55), 349.0 (4.78), 266.0 (4.42), 228.0 (4.93).

*Anal.* Calcd. for C<sub>56</sub>H<sub>28</sub>N<sub>9</sub>F<sub>36</sub>O<sub>13</sub>V (1755.77): C, 38.31; H, 1.61; N, 6.38; F, 38.95. Found: C, 38.34; H, 1.55; N, 6.36; F, 39.21.

## Results and Discussion.

The desired novel unsymmetrical phthalocyanines **2**, **3** and **4** were prepared according to the route shown in Scheme 1. 3,4,5,6-Tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (**1**) was prepared by a modification of the reference method [15]. The nucleophilic substitution reaction of 3,4,5,6-tetrafluorophthalonitrile with 2,2,2-trifluoroethanol in *N,N*-dimethylformamide using potassium carbonate as a base at room temperature for 12 hours gave **1** in 94% yield. The vanadium trichloride-mediated statistical condensation of the two corresponding phthalonitriles with urea as a solvent and co-reactant produced the desired unsymmetrical metallophthalocyanines, and the reaction conditions including feed ratio, temperature and time were varied in order to give an optimal yield of target product. The mixed condensation of a 1:5 molar ratio of compound **1** and 4-nitrophthalonitrile in the presence of an excess of vanadium trichloride and dry urea at 180-190° yielded vanadyl 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecakis(2,2,2-trifluoroethoxy)phthalocyaninate, **2** and other statistical mixtures. Because of the large difference in solubility between compound **1** and 4-nitrophthalonitrile, the R<sub>f</sub> values of these different product moieties on thin layer chromatography (tlc) (silica gel; hexane/ethyl acetate, 3:1, v: v) were in the order of vanadyl hexadecakis(2,2,2-trifluoroethoxy)phthalocyaninate > **2** > other statistical mixtures. Thus unsymmetrical phthalocyanine **2** could be relatively easily separated by common column chromatography using hexane/ethyl acetate as eluent and obtained in 16% yield. Similarly, compound **3** was prepared by a statistical condensation of

a 1:7 molar ratio of **1** and 4-aminophthalonitrile at 180-200°, and obtained in 3.7% yield after purification. Compound **4** was also synthesized by a similar mixed condensation of a 1:5 molar ratio of **1** and phthalonitrile in 10% yield. However, different from **2** and **3**, compound **4** was eluted first in the first-round separation by column chromatography. The fact that the yield of unsymmetrical phthalocyanine differs with the different substituent can be attributed to the different reactivity of 4-substituted phthalonitrile, which is related to the melting point temperature and the electron-density of the benzene ring of 4-substituted phthalonitrile.

We have also tried to synthesize the target compound **2** by mixed condensation of the two corresponding 1,3-diiminoindolines, but this method was not successful because 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile could not be smoothly converted to the corresponding 1,3-diiminoindoline when reacted with ammonia gas in the presence of sodium methoxide in methanol or other alcohols [16].

All the pure final products were obtained after purified by column chromatography on silica gel for several times and then recrystallized from ethyl acetate-hexane. They were characterized by <sup>1</sup>H-nmr, ir and fast-atom-bombardment ms spectroscopic methods, as well as by elemental analysis. All the analytical and spectra data are consistent with the predicted structures. It should be noted that the <sup>1</sup>H nmr spectra of these unsymmetrical vanadylphthalocyanines are extremely broad because of the presence of the paramagnetic vanadium atom and the constitutional isomers [17]. Owing to the broad <sup>1</sup>H nmr spectra of these unsymmetrical phthalocyanines, the aromatic protons can not be expected to be clearly resolved. Attempts to record the well-resolved <sup>13</sup>C nmr spectra of these unsymmetrical vanadylphthalocyanines were not successful.

All unsymmetrical phthalocyanines **2**, **3** and **4** show good solubility in common organic solvents such as diethyl ether, tetrahydrofuran, ethyl acetate and acetone. However, among these unsymmetrical phthalocyanines, **3** shows the best solubility in less polar solvent such as toluene and chloroform.

The uv/visible absorption spectra of compounds **2**, **3** and **4** in 1,4-dioxane are given in Figure 1. All three new unsymmetrical phthalocyanines show characteristic absorptions in the Q-band region of around 730 nm without splitting. Compared with nitro-substituted compound **2**, compound **3** shows a slightly red-shifted Q-band, due to the different contribution of electron-donating amino and electron-withdrawing nitro group to the phthalocyanine ring  $\pi$ -conjugation, while compound **4** shows an absorption spectrum quite similar to that of compound **2**. However, compound **3** was demonstrated to be more aggregated in 1,4-dioxane than compounds **2** and **4** not only by the broadening of the

Q-band with a shoulder on the longer wavelength side but also by the absorption in the window region between 450 and 600 nm. The latter phenomenon is quite unique because tris(*tert*-butyl) or hexakis(*n*-hexyloxy)-substituted mono-amino unsymmetrical phthalocyanines do not show such kind of behavior in the optical window region [6d,6f]. These interesting facts might be attributed to the existence of strong intermolecular aggregation of compound **3** in polar solvent like 1,4-dioxane. The amino group may interact with the fluorine atoms of 2,2,2-trifluoroethoxy group through hydrogen-bonding, which causes the strong aggregation between compound **3** molecules. This result may account for the broadening of Q-band and the absorption in the window region between 450 and 600 nm.

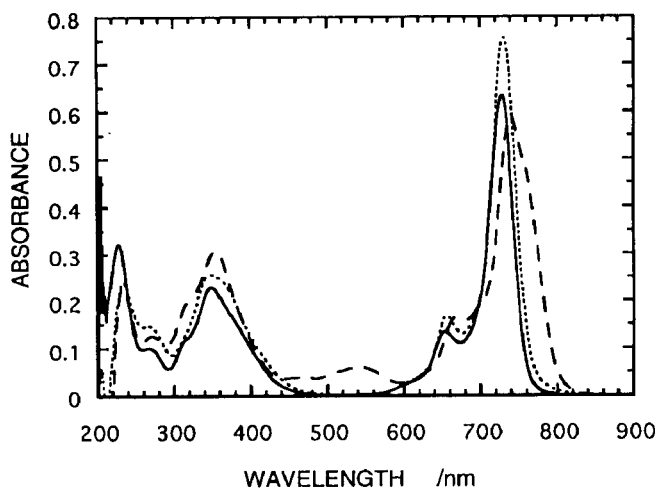


Figure 1. Ultraviolet-visible absorption spectra of vanadyl 23-nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodeca(2,2,2-trifluoroethoxy)phthalocyaninate **2** (.....), vanadyl 23-amino-1,2,3,4,8,9,10,11,15,16,17,18-dodeca(2,2,2-trifluoroethoxy)phthalocyaninate **3** (---) and vanadyl 1,2,3,4,8,9,10,11,15,16,17,18-dodeca(2,2,2-trifluoroethoxy)phthalocyaninate **4** (—) in 1,4-dioxane.

Figures 2 and 3 show the absorption spectra for poly(methyl methacrylate) films doped with various concentrations of compound **2** or **3** normalized by the peak value. Mononuclear phthalocyanine generally shows no sign of intermolecular aggregation in common solvents at concentration below  $1 \times 10^{-5}$  M at room temperature [18]. At higher concentration, however, intermolecular aggregation can occur. In Figures 2 and 3, the concentration in chloroform solution of compound **2** or **3** is lower than  $1 \times 10^{-5}$  M and then the spectrum for chloroform solution represents non-aggregated or "monomeric" state. On the other hand, pure film obtained by spin-coating of chloroform solution without poly(methyl methacrylate) shows the fully aggregated state. Both compounds **2** and **3** showed aggregation effect to some extent in solid state, and the aggregation

effect grows slightly with the increase of doped concentration. However, compared with tetrakis(*tert*-butyl) metal free phthalocyanine [19], neither **2** nor **3** showed significant blue-shift of Q-band with the concentration in solid state increased. This result can be explained from the dodecakis(2,2,2-trifluoroethoxy)-substitution of phthalocyanine ring. The strong repulsion effect of fluoro atoms reduces the possibility of the severe aggregation between phthalocyanine molecules in solid state. The aggregation properties of compound **4** in the solid state was similar to compound **2**, just as demonstrated in 1,4-dioxane solution.

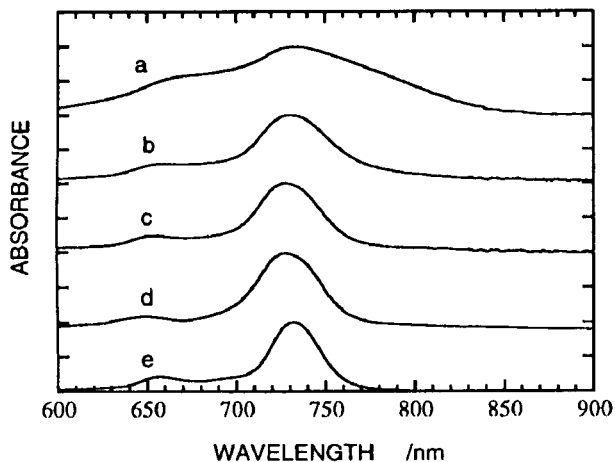


Figure 2. Ultraviolet-visible absorption spectra of vanadyl 23-nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodeca(2,2,2-trifluoroethoxy)phthalocyaninate **2** in solution and in doped poly(methyl methacrylate) films: a, neat film without polymer; b, doped concentration 10% (weight); c, doped concentration 1% (weight); d, doped concentration 0.1% (weight); e, chloroform solution.

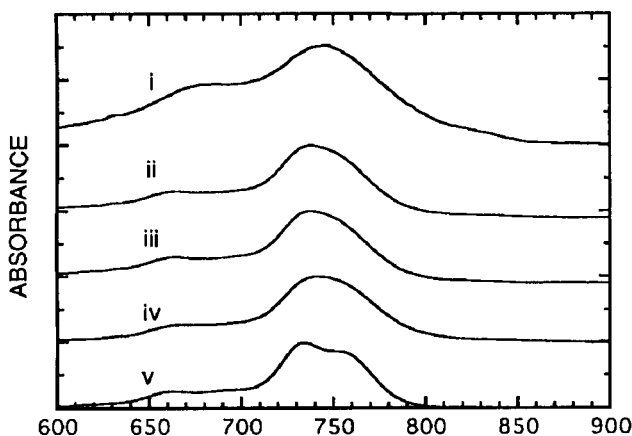


Figure 3. Ultraviolet-visible absorption spectra of vanadyl 23-amino-1,2,3,4,8,9,10,11,15,16,17,18-dodeca(2,2,2-trifluoroethoxy)phthalocyaninate **3** in solution and in doped poly(methyl methacrylate) films: i, neat film without polymer; ii, doped concentration 10% (weight); iii, doped concentration 1% (weight); iv, doped concentration 0.1% (weight); v, chloroform solution.

In summary, three novel unsymmetrical dodecakis(2,2,2-trifluoroethoxy)vanadylphthalocyanines with 23-nitro or 23-amino substituents as well as with the 23-position unsubstituted were synthesized by a statistical condensation reaction, separated by common column chromatography and fully characterized. Besides, their uv-visible absorption spectra in solution and in doped polymer films showed that they were less aggregated phthalocyanines. The introduction of poly 2,2,2-trifluoroethoxy groups enhances the solubility of these new unsymmetrical phthalocyanines, makes the separation more easy, and suppresses the intermolecular aggregation effect. The study of their photoconductive, non-linear optical and other physical and chemical properties is now in progress and the results will be published elsewhere.

#### REFERENCES AND NOTES

- \* To whom correspondence should be addressed.
- [1] F. H. Moser and A. L. Thomas, *The Phthalocyanines*, Vols I and II, CRC Press, Boca Raton, Florida, 1983.
  - [2] C. C. Leznoff and A. B. P. Lever, ed, *Phthalocyanines, Properties and Applications*, Vols I, II, and III, VCH Publishers, Inc, Weinheim, New York, 1989, 1993, 1993.
  - [3a] H. Schultz, H. Lehmann, M. Rein and M. Hanack, *Struct. Bonding (Berlin)*, **74**, 41 (1990); [b] M. Hanack and M. Lang, *Advan. Mater.*, **6**, 819 (1994).
  - [4a] C. Piechocki and J. Simon, *J. Chem. Soc., Chem. Commun.*, 259 (1985); [b] J. F. Van der Pol, E. Neeleman, R. J. M. Nolte, Z. W. Zwikker and W. Drenth, *Makromol. Chem.*, **190**, 2727 (1989); [c] G. C. Bryant, M. J. Cook, S. D. Haslam, R. M. Richardson, T. G. Ryan and A. J. Thorne, *J. Mater. Chem.*, **4**, 209 (1994); [d] M. J. Cook, G. Cooke and A. Jafari-Fini, *J. Chem. Soc., Chem. Commun.*, 1715 (1995); [e] G. J. Clarkson, N. B. McKeown and K. E. Treacher, *J. Chem. Soc., Perkin Trans. 1*, 1817 (1995); [f] G. C. Bryant, M. J. Cook, T. G. Ryan and A. J. Thorne, *Tetrahedron*, **52**, 809 (1996).
  - [5a] D. Q. Li, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, **110**, 1707 (1988); [b] Y. Q. Liu, Y. Xu, D. B. Zhu, T. Wada, H. Sasabe, L. Y. Liu and W. C. Wang, *Thin Solid Films*, **244**, 943 (1994); [c] Y. Q. Liu, Y. Xu, D. B. Zhu, T. Wada, H. Sasabe, X. S. Zhao and X. M. Xie, *J. Phys. Chem.*, **99**, 6957 (1995).
  - [6a] I. Rosenthal, *Photochem. Photobiol.*, **53**, 859 (1991); [b] J. W. Winkelman, D. Arad and S. Kimel, *J. Photochem. Photobiol. B. Biol.*, **18**, 181 (1993); [c] T. J. Dougherty, *Photochem. Photobiol.*, **58**, 895 (1993); [d] S. V. Kudrevish, H. Ali and J. E. van Lier, *J. Chem. Soc., Perkin Trans. 1*, 2767 (1994); [e] J. Morgan, H. Lottman, C. C. Abbou and D. K. Chopin, *Photochem. Photobiol.*, **60**, 486 (1994); [f] H. Kliesh, A. Weitemeyer, S. Müller and D. Wöhrle, *Liebigs Ann. Chem.*, 1269 (1995).
  - [7a] M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 1148 (1987); [b] M. J. Cook, N. B. McKeown, J. M. Simmons, A. J. Thomson, M. F. Daniel, K. J. Harrison, R. M. Richardson and S. J. Roser, *J. Mater. Chem.*, **1**, 121 (1991); [c] I. Chambrier, M. J. Cook, S. J. Cracknell and J. McMurdo, *J. Mater. Chem.*, **3**, 841 (1993); [d] M. J. Cook, J. McMurdo, D. A. Miles, R. H. Poynter, J. M. Simmons, S. D. Haslam, R. M. Richardson and K. Welford, *J. Mater. Chem.*, **4**, 1205 (1994); [e] G. C. Bryant, M. J. Cook, C. Ruggiero, T. G. Ryan and A. J. Thorne, S. D. Haslam and R. M. Richardson, *Thin Solid Films*, **243**, 316 (1994); [f] R. H. Poynter, M. J. Cook, M. A. Chesters, D. A. Slater, J. McMurdo and K. Welford, *Thin Solid Films*, **243**, 346 (1994); [g] Y. Gorbunova, M. L. Rodríguez-Méndez, J. Souto, L. Tomilova and J. A. de Saja, *Chem. Mater.*, **7**, 1443 (1995); [h] I. Chambrier, M. J. Cook and D. A. Russell, *Synthesis*, 1283 (1995).

- [8] M. Kimura, T. Dakeno, E. Adachi, T. Koyama, K. Hanabusa and H. Shirai, *Macromol. Chem. Phys.*, **195**, 2423 (1994).
- [9a] C. C. Leznoff, S. Greenberg, C. R. McArthur and B. Khouw, *Nouv. J. Chim.*, **6**, 653 (1982); [b] C. C. Leznoff and T. W. Hall, *Tetrahedron Letters*, **23**, 3023 (1982); [c] D. Wöhrle and G. Krawczyk, *Polym. Bull.*, **15**, 193 (1986); [d] C. C. Leznoff, P. I. Svirskaya, B. Khouw, R. L. Cerny, P. Seymour and A. B. P. Lever, *J. Org. Chem.*, **56**, 82 (1991).
- [10a] N. Kobayashi, R. Kondo, S. Nakajima and T. Osa, *J. Am. Chem. Soc.*, **112**, 9640 (1990); [b] N. Kobayashi, R. Kondo, T. Ashida, S. Nakajima and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1203 (1991); [c] K. Kasuga, T. Idehara, M. Handa and K. Isa, *Inorg. Chim. Acta*, **196**, 127 (1992); [d] E. Musluoglu, A. Gürek, V. Ahsen, A. Gül and Ö. Bekaroglu, *Chem. Ber.*, **125**, 2337 (1992); [e] S. Dabak, A. Gül, Ö. Bekaroglu, *Chem. Ber.*, **127**, 2009 (1994); [f] A. Weitemeyer, H. Kliesh and D. Wöhrle, *J. Org. Chem.*, **60**, 4900 (1995); [g] A. Sastre, T. Torres and M. Hanack, *Tetrahedron Letters*, **36**, 8501 (1995).
- [11a] C. C. Leznoff, S. Greenberg, B. Khouw and A. B. P. Lever, *Can. J. Chem.*, **65**, 1705 (1987); [b] H. Konami and M. Hatano, *Chem. Letters*, 1359 (1988); [c] C. C. Leznoff and S. Greenberg, *Tetrahedron Letters*, **30**, 5555 (1989); [d] Y. Ikeda, H. Konami, M. Hatano and K. Mochizuki, *Chem. Letters*, 763 (1992); [e] J. Yang, T. C. Rogers and M. R. Van De Mark, *J. Heterocyclic Chem.*, **30**, 571 (1993); [f] C. C. Leznoff, C. R. McArthur, Y. Qin, *Can. J. Chem.*, **71**, 1319 (1993); [g] J. Vacus, G. Memetizidis, P. Doppelt and J. Simon, *J. Chem. Soc., Chem. Commun.*, 697 (1994); [h] Y. Q. Liu, D. B. Zhu, T. Wada, A. Yamada and H. Sasabe, *J. Heterocyclic Chem.*, **31**, 1017 (1994); [i] T. G. LinlBen and M. Hanack, *Chem. Ber.*, **127**, 2051 (1994); [j] Y. Q. Liu and D. B. Zhu, *Synth. Metals*, **71**, 1853 (1995); [k] K. E. Treacher, G. J. Clarkson, Z. Ali-Adib and N. B. McKeown, *Chem. Commun.*, 73 (1996); [l] N. Kobayashi, M. Togashi, T. Osa, K. Ishii, S. Yamauchi and H. Hino, *J. Am. Chem. Soc.*, **118**, 1073 (1996).
- [12] N. Kobayashi, T. Ashida and T. Osa, *Chem. Letters*, 2031 (1992).
- [13] T. Wada and H. Sasabe, *Proceedings of SPIE-the International Society for Optical Engineering*, **2143**, 164 (1994).
- [14] T. Wada, Y. Matsuoka, K. Shigehara, A. Yamada, A. F. Garito and H. Sasabe, *Proceedings of Materials Research Society - International Meeting on Advanced Materials, MRS Tokyo*, **12**, 75 (1989).
- [15] H. Kobayashi, K. Matsumoto and T. Sonoda, *Proceedings of the 2nd International Symposium on the Chemistry of Functional Dyes, Kobe, 1992*, Mita Press, Osaka, Japan, Abstracts, pp 290.
- [16] P. J. Brach, S. J. Grammatica, O. A. Ossanna and L. Weinberger, *J. Heterocyclic Chem.*, **7**, 1403 (1970).
- [17] K.-Y. Law, *Inorg. Chem.*, **24**, 1778 (1985).
- [18] E. S. Dodsworth, A. B. P. Lever, P. Seymour and C. C. Leznoff, *J. Phys. Chem.*, **89**, 5698 (1985).
- [19] S. Yanagi, T. Wada, J. Kumar, H. Sasabe and K. Sasaki, *Mol. Cryst. Liq. Cryst.*, **255**, 167 (1994).