Syntheses of New Unsymmetrically Dodecakis(trifluoroethoxy)-Substituted Metallophthalocyanines by a Palladium-catalyzed Cross-coupling Reaction

Minquan Tian† [a], Tatsuo Wada* [a,b] and Hiroyuki Sasabe [b,c]

[a] Supramolecular Science Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan [b] Core Research for Evolutional Science and Technology (CREST), RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan [c] Department of Photonic Materials Science, Chitose Institute of Science and Technology, 758-65 Bibi, Chitose, Hokkaido 066-8655, Japan

Received June 10, 1999

Novel unsymmetrical vanadyl and zinc dodecakis(2,2,2-trifluoroethoxy)phthalocyaninates with an iodo group were synthesized by a statistical condensation route. The palladium-catalyzed coupling reaction between such monoiodinated metallophthalocyanines and terminal acetylenic derivatives gave various new unsymmetrically dodecakis(2,2,2-trifluoroethoxy)-substituted metallophthalocyanines with extended exocyclic π-conjugation. Unsymmetrical zinc dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate with a nitro group was also prepared for comparison. All the target phthalocyanines were separated by common column chromatography and characterized by elemental analysis, ir and ^{1}H-nmr, uv-visible and fast-atom-bombardment mass spectroscopy.

J. Heterocyclic Chem., **37**, 1193 (2000).

Introduction.

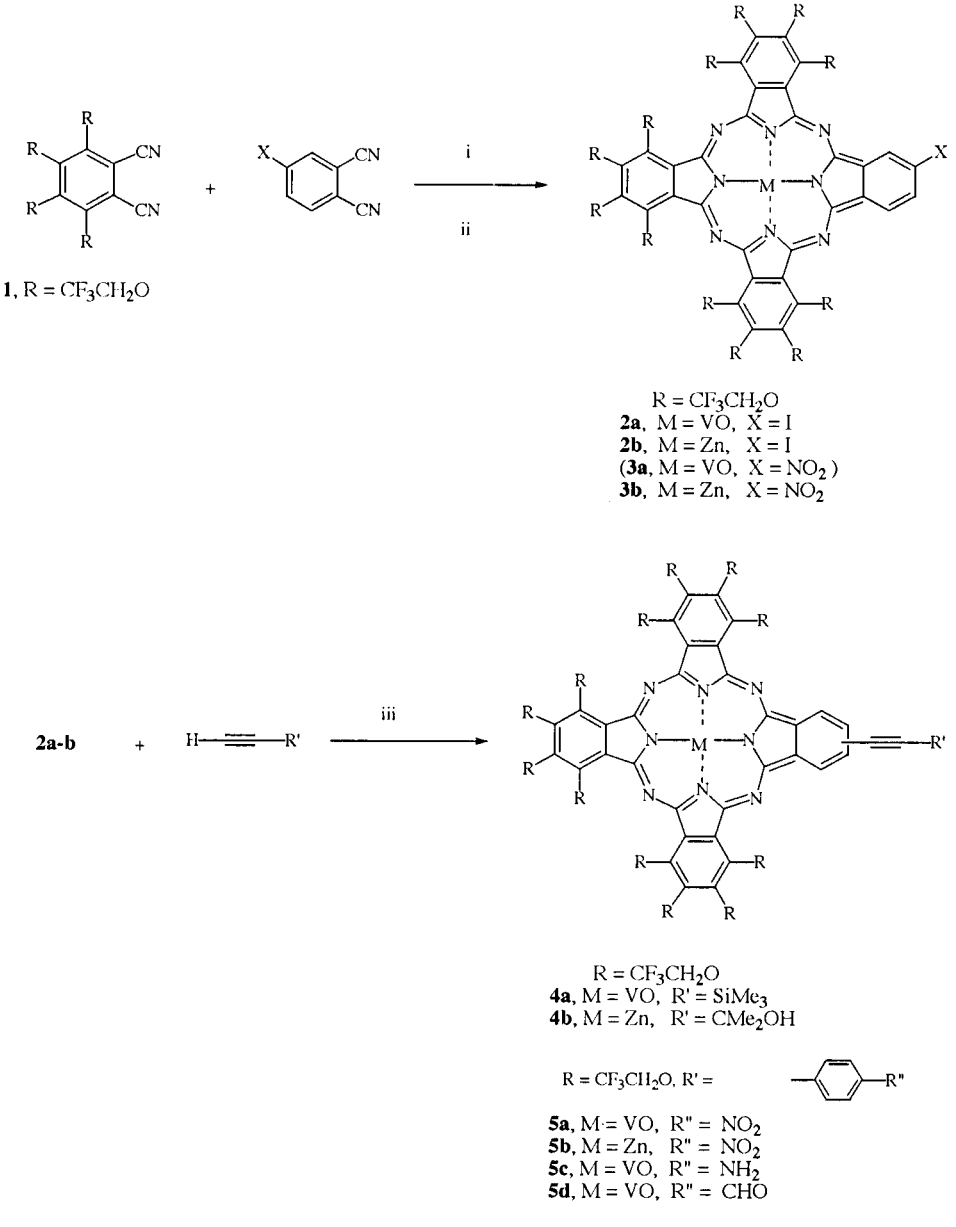
Phthalocyanines are a class of two-dimensional π-conjugated aromatic macrocycles which exhibit a number of unique properties and have found practical applications in many fields such as dyes, catalysts, chemical sensors, liquid crystals and nonlinear optics [1-3]. To date a great variety of symmetrical or pseudosymmetrical phthalocyanines have been prepared for basic research and industrial applications [1-3]. However, much less effort has been devoted to the investigation of the properties of unsymmetrically substituted phthalocyanines, mainly because they are much more difficult to synthesize and purify. Recently, unsymmetrical phthalocyanines have attracted increasing research attention in the field of liquid crystals [4], Langmuir-Blodgett (LB) film formation [5], photodynamic therapy of cancer [6], and second-order nonlinear optics [7]. In particular, monofunctional phthalocyanines with only one reactive functional group such as one sulfo, carboxyl, amino or hydroxyl group are much more attractive [4b,4f,6d,6f,8], because they are intermediates for many novel unsymmetrical phthalocyanines which may possess some new properties. Moreover, such monofunctional phthalocyanines have the advantage of polymer binding without the disadvantage of crosslinking reactions. For example, they can be bound to biomolecules like monoclonal antibodies to form a new group of photosensitizers for the photodynamic therapy of cancer.

Although symmetrical phthalocyanines can be prepared straightforwardly from the appropriately substituted phthalonitriles, there are few efficient methods to prepare unsymmetrical phthalocyanines. Methods for the synthesis of unsymmetrical phthalocyanines are: (i) the statistical condensation of two differently substituted phthalonitriles or corresponding 1,3-diiminoisoindolines [9], (ii) the polymer support route [10], and (iii) the ring enlargement reaction of subphthalocyanines through a condensation with substituted 1,3-diiminoisoindoline [7d,11]. Other more specific methods such as stepwise synthetic procedures [12], the mixed condensation of two different phthalyl precursors [13] and a route including modified Meerwein reaction conditions [6d] have also been used to prepare unsymmetrical phthalocyanines and their analogues. Each method has its advantages and disadvantages, and the applicability of each method depends strongly on the nature of the substituents on the phthalocyanine ring, the central metal ion, the reactivity of the precursors, the solvent as well as other factors. In short, none of the methods can be considered to be perfect. Therefore it is still necessary to explore more efficient methods for the preparation of unsymmetrical phthalocyanines, especially monofunctional phthalocyanines.

Unsymmetrical phthalocyanines with peripheral donor and acceptor substituents have been theoretically proposed as novel materials for second-order nonlinear optics [7a]. However, only a limited number of reports on this research subject are available [7b,7c,7d,9h]. On the other hand, it is well known that the palladium-catalyzed coupling of aryl and alkenyl halides with terminal alkynes is a widely used reaction in organic synthesis [14]. Nevertheless, to our knowledge, there have been very few reports on such kind of coupling reaction involving halogenated phthalocyanine [8b]. Recently, we have reported the preliminary result of the synthesis of some novel non-aggregated unsymmetrical metallophthalocyanines for second-order nonlinear optics using a palladium-catalyzed cross-coupling reaction [15]. Here we report the detailed

results of the convenient synthesis of a series of new unsymmetrically dodecakis(2,2,2-trifluoroethoxy)-substituted metallophthalocyanines with extended exocyclic π-conjugation by the palladium(0)-catalyzed cross-coupling reaction between monoiodinated phthalocyanines and terminal acetylenes (see Scheme 1). There are several molecular aggregation. Secondly, the introduction of different functional substituents like iodo, 2-trimethylsilylethynyl, exocyclic conjugated amino or formyl group at the comparable position on one of the benzene units would provide useful intermediates for the syntheses of many new mononuclear, binuclear and polynuclear

Scheme 1



Reagents and conditions: i, vanadium trichloride (or zinc chloride), urea, 180-205°, 3-5 hours; ii, H^+/water, reflux, 2-4 hours; iii, bis(triphenylphosphine)-palladium chloride/copper(I) iodide, triethylamine/tetrahydrofuran, 25-40°, 24-48 hours.

reasons why we designed and synthesized such unsymmetrical phthalocyanines. First, we introduced twelve 2,2,2-trifluoroethoxy groups on three of the benzene units in order to enhance the solubility and suppress the intermolecular aggregation. Secondly, the introduction of different functional substituents like iodo, 2-trimethylsilylethynyl, exocyclic conjugated amino or formyl group at the comparable position on one of the benzene units would provide useful intermediates for the syntheses of many new mononuclear, binuclear and polynuclear phthalocyanines. On the other hand, we expect those target unsymmetrical phthalocyanines with twelve 2,2,2-trifluoroethoxy groups as donor substituents and a nitro or an exocyclic conjugated nitro group as an acceptor

substituent to be good candidates for second-order nonlinear optics. Moreover, the different central metal ions are also very important in understanding the nonlinear optical properties of phthalocyanines [16]. The present paper describes the preparation, characterization and spectral properties of these novel unsymmetrical phthalocyanines.

Results and Discussion.

The desired novel unsymmetrical metallophthalocyanines **2a**, **2b** and **3b** were prepared according to the route shown in Scheme 1. The preparation of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (**1**) was published in our previous study [20] and other groups' work [21,22]. 4-Iodophthalonitrile, one of the starting materials, was prepared by the reference method [23]. The metal salt-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 1:3 molar ratio of compound **1** and 4-iodophthalonitrile 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, **2a** and other statistical phthalocyanine mixtures. The first-round separation by common column chromatography on silica gel with hexane/ethyl acetate (4:1, volume ratio) as an eluent gave the target phthalocyanine **2a** as the first fraction. Compound **2a** was further purified by column chromatography using hexane/ethyl acetate as an eluent and obtained in 23.0% yield. It was found later that the statistical condensation of a 1:1 molar ratio of **1** and 4-iodophthalonitrile gave compound **2a** in a little better yield (25.0%). Similarly, compound **2b** was prepared by a statistical condensation of a 1:1 molar ratio of **1** and 4-iodophthalonitrile in the presence of an excess of zinc chloride and dry urea at 195-205°, and obtained in 15.0% yield after purification. However, quite unlike compound **2a**, compound **2b** was eluted as the third fraction in the first-round separation by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent.

We have also tried to synthesize metal-free 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyanine by a mixed condensation of the two corresponding 1,3-diiminoisoindolines in 2-(*N,N*-dimethylamino)ethanol, 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-diiminoisoindoline when reacted with ammonia gas in the presence of sodium methoxide in methanol or other alcohols [24].

Previously we have reported the synthesis of unsymmetrical phthalocyanine **3a** for second-order nonlinear optics [20]. For a comparison study, we also prepared the analogue **3b** by a similar procedure depicted in Scheme 1. The mixed condensation of a 1:5 molar ratio of compound **1** and 4-nitrophthalonitrile in the presence of an excess of zinc chloride and dry urea at 195-205° yielded zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecakis(2,2,2-trifluoroethoxy)phthalocyaninate, **3b** and other statistical product mixtures. The target phthalocyanine **3b** was separated by common column chromatography using hexane/ethyl acetate as an eluent and obtained in 18.1% yield. However, quite unlike compound **3a**, compound **3b** was eluted first in the first-round separation by column chromatography on silica gel with hexane/ethyl acetate (1:1) as an eluent. It was also noted that the mixed condensation of compound **1** and 4-nitrophthalonitrile in the presence of an excess of zinc chloride and dry urea could not take place at a temperature below 190°.

Compounds **2a** and **2b** are new monofunctional phthalocyanines with one reactive iodo group. They can be expected to be useful in the palladium-catalyzed coupling with terminal alkynes [14]. Recently the Heck type coupling of halogenated porphyrin with monosubstituted acetylenes has been reported [25]. While our work was in progress, another group reported a similar approach [8b].

Scheme 1 shows the synthesis of 23-(2-substituted-ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl and zinc complexes (**4a-b** and **5a-d**) by the palladium(0)-catalyzed cross-coupling reaction. The intermediates 4-nitrophenylacetylene [17], 4-aminophenylacetylene [17] and 4-formylphenylacetylene [18] were prepared according to the reference methods. The monoiodinated unsymmetrical phthalocyanines **2a** and **2b** were treated with a range of monosubstituted acetylenes in triethylamine-tetrahydrofuran (1:1, volume ratio) in the presence of catalytic quantities of bis(triphenylphosphine)palladium chloride and copper(I) iodide under a dry nitrogen atmosphere (Scheme 1). All the monosubstituted acetylenes treated in this way reacted smoothly to give the corresponding 23-(2-substituted-ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl and zinc complexes **4a-b** and **5a-d** in 75-95% yields. Better yield was obtained when the coupling reaction was carried out at lower temperature. Since the terminal alkynes were in large excess and the coupling reaction was carried out for sufficient time, the monoiodinated unsymmetrical phthalocyanine **2a** or **2b** was converted completely. This fact makes fast purification and isolation of products possible. As can be seen from the diversity of substituted alkynes which undergo this reaction, the

method is a powerful tool for attaching substituents to a phthalocyanine through a common acetylenic linkage to give new unsymmetrical phthalocyanine derivatives. In particular, biologically active moieties, or moieties with unique electro-optical, magnetical, or nonlinear optical properties can be attached to a phthalocyanine to afford new advanced materials. The fact that the coupling was carried out under mild conditions of low temperature and ambient pressure also makes it attractive for the incorporation of sensitive organic functional groups, as demonstrated by the linking of 4-formylphenylacetylene with **2a**.

All final products were obtained as pure samples after numerous purifications *via* column chromatography on silica gel and then by recrystallization. They were characterized by ^{1}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 ^{1}H-nmr spectra of unsymmetrical vanadylphthalocyanines are extremely broad because of the presence of the paramagnetic vanadium atom and the constitutional isomers [26]. Owing to the broad ^{1}H-nmr spectra, the aromatic protons of those unsymmetrical vanadylphthalocyanines can not be expected to be clearly resolved. Attempts to record the well-resolved ^{13}C-nmr spectra of those unsymmetrical vanadylphthalocyanines were not successful. On the other hand, the ^{1}H-nmr spectra of unsymmetrical zincphthalocyanines are better resolved than those of unsymmetrical vanadylphthalocyanines due to the diamagnetism of zinc atom.

All dodecakis(2,2,2-trifluoroethoxy)-substituted unsymmetrical metallophthalocyanines **2a-b, 3b, 4a-b** and **5a-d** show good solubility in common polar organic solvents such as diethyl ether, tetrahydrofuran, ethyl acetate and acetone. It was noted that unsymmetrical zincphthalocyanines **2b, 3b** and **5b** showed better solubility in more polar solvents like methanol and ethanol than the corresponding vanadylphthalocyanines **2a, 3a** and **5a**. However, among these unsymmetrical phthalocyanines, **5c** shows the best solubility in less polar solvents such as toluene and chloroform.

The uv/visible absorption spectra of compounds **2a** and **2b** in 1,4-dioxane are given in Figure 1. The novel monoiodinated unsymmetrical vanadylphthalocyanine **2a** shows characteristic absorptions in the Q-band region of around 728.5 nm without splitting and in the B-band region of around 352 nm, while the new monoiodinated unsymmetrical zincphthalocyanine **2b** exhibits characteristic absorptions in the Q-band region of around 699.5 nm without splitting and in the B-band region of around 360 nm. Compared with the corresponding compound **2b**, compound **2a** shows a similar-shaped Q-band but with a red-shift of 29 nm. This result can be explained from the molecular structure of phthalocyanine. Compounds **2a** and **2b** have the same peripheral substitution of the phthalocyanine ring but different central metal ions. The same peripheral substitution leads to the similar shape of their Q-bands. However, the unfilled *d*-orbitals and the axial substitution on the central vanadium atom of compound **2a** can be expected to make a much larger positive contribution to the phthalocyanine ring π-conjugation than the saturated *d*-orbitals on the zinc atom of compound **2b** without axial substitution. Since the Q-band absorption results from the $\pi \rightarrow \pi^*$ transition [27], the unsymmetrical vanadylphthalocyanine **2a** would show a considerable bathochromic shift of the Q-band in comparison with the corresponding zincphthalocyanine **2b**.

Figure 2 shows the uv/visible absorption spectra of compounds **3a** and **3b** in 1,4-dioxane. Compound **3a**

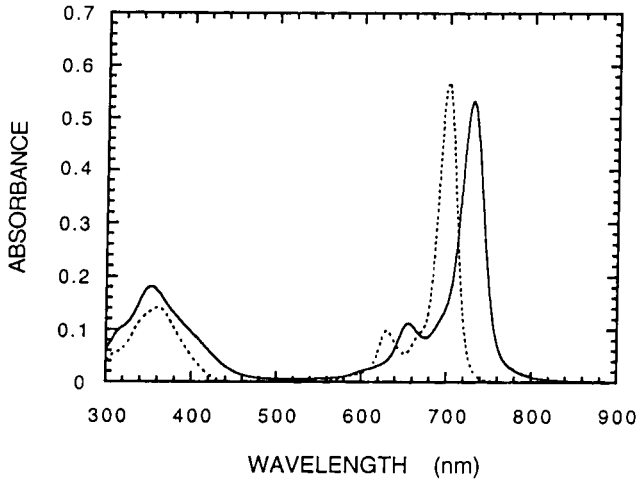


Figure 1. Ultraviolet-visible absorption spectra of vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **2a** (—) and zinc 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **2b** (·····) in 1,4-dioxane.

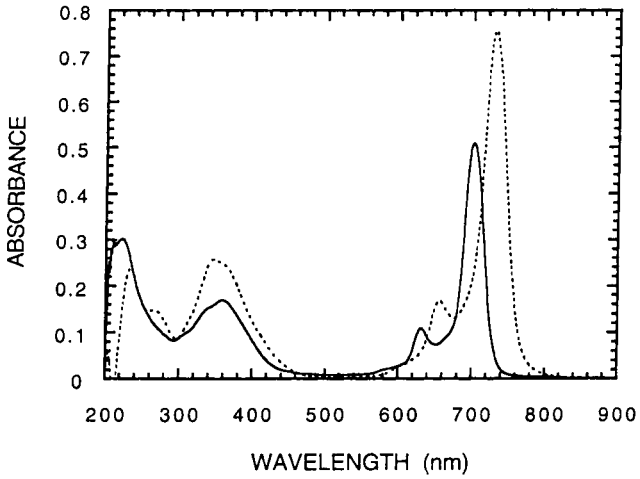


Figure 2. Ultraviolet-visible absorption spectra of vanadyl 23-nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **3a** (·····) and zinc 23-nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **3b** (—) in 1,4-dioxane.

shows characteristic absorptions in the Q-band region of around 730 nm without splitting and in the B-band region of around 347 nm [20], while the new unsymmetrical zincphthalocyanine **3b** exhibits typical absorptions in the Q-band region of around 701 nm without splitting and in the B-band region of around 360 nm. Compared with the corresponding vanadylphthalocyanine **3a**, compound **3b** shows a similar-shaped Q-band but with a blue-shift of 29 nm, as expected.

Figures 3 and 4 show the uv/visible absorption spectra of compounds **4a-b** and **5a-d** in 1,4-dioxane, respectively. Novel unsymmetrical vanadylphthalocyanines **4a**, **5a**, **5c** and **5d** show characteristic absorptions in the Q-band region of around 733 nm without splitting and in the B-band region of around 353 nm, while new unsymmetrical zincphthalocyanines **4b** and **5b** exhibit characteristic absorptions in the Q-band region of around 703 nm without splitting and in the B-band region of around 360 nm. In comparison with compounds **5a** and **5d**, compound **5c** shows a slightly red-shifted Q-band, due to the different contribution of electron-donating amino and electron-withdrawing nitro and formyl groups to the phthalocyanine ring π-conjugation. Moreover, similar to vanadyl 23-amino-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate [20], compound **5c** was demonstrated to be more aggregated in 1,4-dioxane than compounds **5a** and **5d** 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. This fact might be explained by the existence of strong intermolecular aggregation of compound **5c**, which stems from the intermolecular hydrogen-bonding interaction between the amino group and the fluorine atoms of 2,2,2-trifluoroethoxy group in polar solvent like 1,4-dioxane. In contrast to compound **5c**, compounds **5a**, **5b** and **5d** show a transparent window region between 480 and 580 nm in their uv/visible absorption spectra in 1,4-dioxane. This transparent window region is very useful for the second harmonic generation research. On the other hand, compounds **5a** and **5b** have an extended exocyclic conjugation when compared with the corresponding compounds **3a** and **3b**. However, only 3-nm red-shifts of Q-band were observed in the uv/visible absorption spectra from compound **3a** to **5a** and from **3b** to **5b**. These results may be explained by the reduction of effective conjugation between the phthalocyanine ring and exocyclic phenyl ring due to the rotation of the benzene ring around the carbon-carbon triple bond.

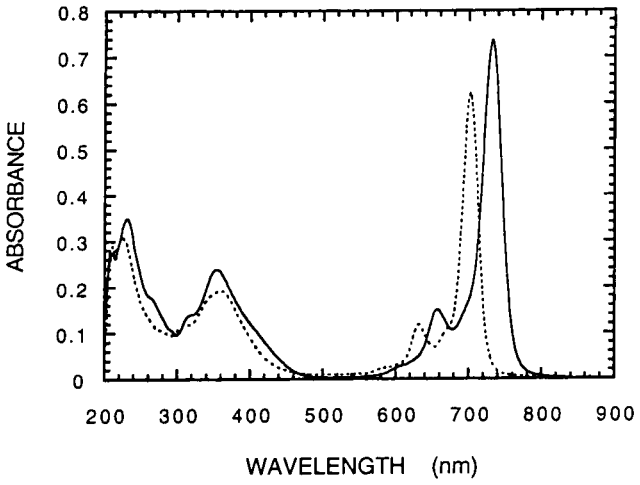


Figure 3. Ultraviolet-visible absorption spectra of vanadyl 23-(2'-trimethylsilylethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **4a** (—) and zinc 23-(3'-hydroxy-3'-methyl-1'-butynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **4b** (·····) in 1,4-dioxane.

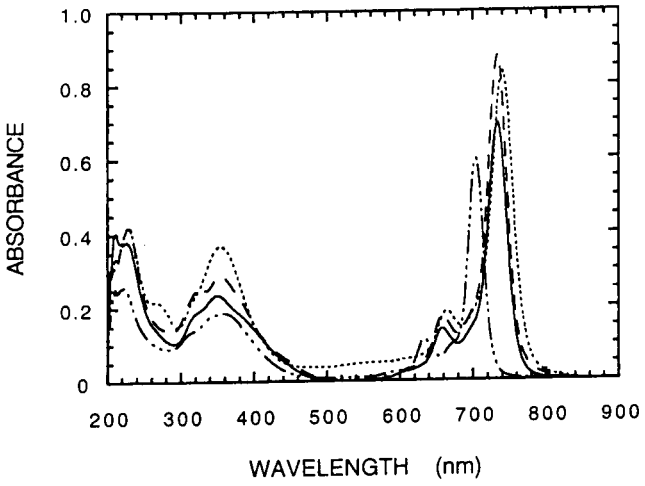


Figure 4. Ultraviolet-visible absorption spectra of vanadyl 23-(2'-(4"-nitrophenyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **5a** (—), zinc 23-(2'-(4"-nitrophenyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **5b** (–···–), vanadyl 23-(2'-(4"-aminophenyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **5c** (·····) and vanadyl 23(-2'-(4"-formylphenyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **5d** (- - - -) in 1,4-dioxane.

In summary, two novel monofunctional phthalocyanines, 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl and zinc complexes, and zinc 23-nitro-1,2,3,4,8,9,10,-11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate were synthesized by a statistical condensation of the two corresponding phthalonitriles in the presence of the corresponding metal chloride and urea. The palladium(0)-catalyzed cross-coupling reaction between such monoiodinated unsymmetrical metallophthalocyanines and mono-substituted acetylenes under mild conditions produced various new unsymmetrical dodecakis(2,2,2-trifluoroethoxy)metallophthalocyanines with extended exocyclic π-conjugation in good yields. All the target

unsymmetrical phthalocyanines were separated by common column chromatography and fully characterized. Their solubility and spectral properties in a certain solvent depends strongly not only on the peripheral substituents but also on the central metal ion. It is demonstrated that the application of the palladium(0)-catalyzed coupling method greatly simplifies the preparation of new unsymmetrical phthalocyanine derivatives. Second harmonic generation of spin-coated thin films of poly(methyl methacrylate) doped with those target unsymmetrical metallophthalocyanines containing donor and acceptor groups was observed after electric poling at 110° for 30 minutes at a fundamental wavelength of 1.064 μm [15]. The detailed results of their second-order nonlinear optical and other physical and chemical properties will be published elsewhere.

EXPERIMENTAL

The ir spectra were recorded on a Shimadzu FTIR-4100 Fourier transform infrared spectrophotometer, using potassium bromide pellets. The ^{1}H-nmr and ^{13}C-nmr spectra with tetramethylsilane as 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 RIKEN (The Institute of Physical and Chemical Research). The uv-visible absorption spectra were measured by 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. 4-Nitrophthalonitrile (98%) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Anhydrous tetrahydrofuran was purchased from Kanto Chemical Co., Inc.. Triethylamine was refluxed with sodium chips and distilled in an atmosphere of dry nitrogen gas before use. The solvents for uv-visible absorption measurement were of spectral grade and used without further purification. Other chemicals were of reagent grade and used as supplied.

4-Nitrophenylacetylene [17], 4-aminophenylacetylene [17] and 4-formylphenylacetylene [18] were prepared according to the reference methods. Bis(triphenylphosphine)palladium chloride was prepared according to the literature [19]. 3,4,5,6-Tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (**1**) was prepared according to the procedure published previously [20].

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

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-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (2.60 g, 5.0 mmoles) and 4-iodophthalonitrile (3.81 g, 15 mmoles). To this mixture, were added vanadium trichloride (2.0 g, 12.7 mmoles) and dry urea (30 g) under dry nitrogen gas. The resulting mixture was heated at 110-120° for 1 hour in an atmosphere of dry nitrogen gas, and then heated to 180°, stirred at 180-190° for 4 hours. A dark green solid was formed in the process of reaction. The reaction mixture was then cooled to room temperature, and refluxed with 150 ml of 2% aqueous hydrochloric acid for 4 hours, and then cooled to room temperature. The resulting dark 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 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 4:1 (volume ratio) hexane/ethyl acetate as an eluent. The first green fraction was collected, condensed and further purified by column chromatography on silica gel with hexane/ethyl acetate (5:1, volume ratio) as an eluent (twice), and then with hexane/ethyl acetate (6:1, volume ratio) as the first eluent to remove the front-running yellow impurities, followed by eluting with hexane/ethyl acetate (5:1, volume ratio) to give a dark green solid which was checked by fast-atom-bombardment mass spectroscopy to be **2a**. Recrystallization from ethyl acetate-hexane (1:40) yielded a green microcrystalline solid, 720 mg (23.0%); ir: ν_{max} 3092 (=CH), 2971 (CH_2), 1634, 1630 (C=C ring), 1489 (C=C ring), 1456, 1427 (CH_2), 1406, 1277, 1248 (C-O), 1157 (C-F), 1117 (ring), 1069, 1011, 974 (C-O), 853 (CH_2), 833, 760, 662, 550 (C-I) cm^{-1}; ^{1}H nmr (acetone-d_6): δ 5.24 (m, 16H, OCH_2), 5.50-6.30 (br m, 8H, OCH_2), 7.60-7.80 (br, H_{arom}); ms: fast-atom-bombardment m/z 1881.9 (M^+, 100), 1798.9 (M^+ - CF_3CH_2, 39.5), 1715.9 (M^+ - 2 x CF_3CH_2, 12.4); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/dm^{3}mol^{-1}cm^{-1}] 728.5 (5.25), 655.0 (4.58), 352.0 (4.78), 264.5 (4.51), 228.5 (4.91).

Anal. Calcd. for $C_{56}H_{27}N_8F_{36}O_{13}IV$ (1881.66): C, 35.75; H, 1.45; N, 5.96; F, 36.35. Found: C, 35.92; H, 1.46; N, 5.86; F, 36.46.

Zinc 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**2b**).

To a mixture of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (1.56 g, 3.0 mmoles) and 4-iodophthalonitrile (762 mg, 3.0 mmoles), under dry nitrogen gas, were added zinc chloride (850 mg, 6.0 mmoles) and dry urea (15 g). The resulting mixture was stirred and heated at a temperature of 110-120° for 1 hour under dry nitrogen gas, and then heated to 195°, stirred at 195-205° for 4 hours. A dark-green solid was formed in the process of heating. The reaction mixture was then cooled to room temperature, and refluxed with 70 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 until the filtrate became clear. The combined filtrates were condensed and the resulting black-green residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent to remove the first fraction of yellow impurities and the second fraction of blue by-products, and to give the third green fraction consisting largely of **2b**. The crude unsymmetrical product was further purified by column chromatography on silica gel with chloroform as the first eluent and chloroform/tetrahydrofuran (100:1, volume ratio) as the second eluent (twice), and then with

hexane/ethyl acetate (3:1 to 3:2, volume ratio) as an eluent to give a green solid. Recrystallization from ethyl acetate-hexane (1:18) yielded a green microcrystalline solid, 282 mg (15.0%); ir: ν_{max} 3118 (=CH), 2972, 2896 (CH_2), 1626, 1596 (C=C ring), 1487 (C=C ring), 1456, 1433 (CH_2), 1401, 1335, 1275, 1243 (C-O), 1160 (C-F), 1126 (ring), 1069, 1010, 969 (C-O), 911, 853 (CH_2), 831, 754, 662, 549 (C-I) cm^{-1}; ^1H nmr (acetone-d_6): δ 5.18 (m, 12H, 6 x OCH_2), 5.65 (m, 4H, 2 x OCH_2), 5.80 (q, J = 8.58 Hz, 4H, 2 x OCH_2), 5.96 (q, J = 8.58 Hz, 4H, 2 x OCH_2), 8.33 (d, J = 8.50 Hz, 1H, H_{arom}), 8.75 (d, J = 8.50 Hz, 1H, H_{arom}), 9.25 (s, 1H, H_{arom}); ms: fast-atom-bombardment m/z 1877.9 (M^+ -1, 100), 1878.8 (M^+, 87.6, ^{64}Zn-**2b** requires M^+ 1878.7), 1879.8 (M^+ +1, 92.0), 1880.8 (M^+, 70.5, ^{66}Zn-**2b**), 1881.8 (M^+ +1/^{66}Zn-**2b**, M^+/^{67}Zn-**2b**, 70.2), 1882.8 (M^+, 37.7)/1883.8 (M^+ +1, 20.1)(^{68}Zn-**2b**), 1884.8 (M^+, 8.0)(^{70}Zn-**2b**); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 699.5 (5.41), 630.0 (4.65), 360.5 (4.81), 211.0 (5.38).

Anal. Calcd. for $C_{56}H_{27}N_8F_{36}O_{12}IZn$ (1880.11): C, 35.78; H, 1.45; N, 5.96; F, 36.38. Found: C, 35.59; H, 1.41; N, 5.83; F, 36.13.

Zinc 23-nitro-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**3b**).

In a 200-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-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (1.56 g, 3.0 mmoles), 4-nitrophthalonitrile (2.60 g, 15 mmoles), zinc chloride (2.46 g, 18.0 mmoles) and dry urea (23 g). The mixture was stirred and heated at a temperature of 110-120° for 1 hour under dry nitrogen gas, and then heated to 195°, stirred at 195-205° for 3 hours. A dark-green solid was formed in the process of heating. The reaction mixture was then cooled to room temperature, and refluxed with 100 ml of water for 2 hours, and then cooled to room temperature. The resulting dark-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 until the filtrate became clear. The combined filtrates were condensed and the resulting dark green residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as the first eluent to remove the yellow impurities, followed by eluting with 3:2 and 1:1 (volume ratio) hexane/ethyl acetate to remove the pale-green and yellow impurities, and finally with hexane/ethyl acetate (1:2, volume ratio) as an eluent to give a green fraction consisting largely of **3b**. The crude unsymmetrical product was further purified by column chromatography on silica gel twice with hexane/ethyl acetate (1:1 to 1:2, volume ratio) as an eluent, and then once with chloroform/tetrahydrofuran (100:1 to 25:1, volume ratio) to give a green solid. Recrystallization from ethyl acetate-hexane (1:18) yielded a green microcrystalline solid, 325 mg (18.1%); ir: ν_{max} 3118 (=CH), 2974, 2896 (CH_2), 1627, 1587 (C=C ring), 1523 (NO_2), 1487 (C=C ring), 1452, 1429 (CH_2), 1401, 1339 (NO_2), 1274, 1246 (C-O), 1160 (C-F), 1110 (ring), 1065, 1008, 970 (C-O), 853 (CH_2), 805, 757, 664 cm^{-1}; ^1H nmr (acetone-d_6): δ 5.25 (m, 12H, 6 x OCH_2), 5.33-5.55 (m, 4H, 2 x OCH_2), 5.75 (m, 4H, 2 x OCH_2), 6.19 (m, 4H, 2 x OCH_2), 8.43 (d, J = 7.92 Hz, 1H, H_{arom}), 8.72 (d, J = 7.92 Hz, 1H, H_{arom}), 9.20 (s, 1H, H_{arom}); ms: fast-atom-bombardment m/z 1796.9 (M^+ -1, 100), 1797.9 (M^+, 87.2, ^{64}Zn-**3b** requires M^+ 1797.83), 1798.9 (M^+ +1, 95.6), 1799.9 (M^+, 72.9, ^{66}Zn-**3b**), 1800.9 (M^+ +1/^{66}Zn-**3b**, M^+/^{67}Zn-**3b**, 71.3), 1801.9 (M^+, 44.6)/1802.9 (M^+ +1, 21.1)(^{68}Zn-**3b**), 1803.9 (M^+, 8.9, ^{70}Zn-**3b**); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 701.0 (5.33), 631.0 (4.66), 359.5 (4.85), 221.5 (5.10).

Anal. Calcd. for $C_{56}H_{27}N_9F_{36}O_{14}Zn$ (1799.22): C, 37.38; H, 1.51; N, 7.01; F, 38.01. Found: C, 37.13; H, 1.53; N, 6.84; F, 38.30.

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

A typical procedure for coupling reaction: in a 100-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 vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (100 mg, 5.31 x 10^{-2} mmole), bis(triphenylphosphine)palladium dichloride (2.0 mg, 2.85 x 10^{-3} mmole) and copper(I) iodide (1.0 mg, 5.25 x 10^{-3} mmole). To this mixture, under dry nitrogen atmosphere, were added anhydrous tetrahydrofuran (20 ml), anhydrous triethylamine (20 ml) and trimethylsilylacetylene (0.10 ml, ~0.713 mmole). The resulting reaction mixture was stirred at 30-40° under nitrogen gas for 24 hours. The formed precipitate was filtered and washed with tetrahydrofuran. The filtrate was condensed under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, volume ratio) as an eluent to yield a green solid. Recrystallization from ethyl acetate-hexane to give compound **4a** as a green microcrystalline solid, 84.5 mg (85.9%); ir: ν_{max} 3090 (=CH), 2977 (CH_2), 2357 (ethynyl), 1636, 1628, 1624 (C=C ring), 1487 (C=C ring), 1456, 1429 (CH_2), 1275, 1248 (C-O), 1161 (C-F), 1122 (ring), 1067, 1013, 972 (C-O), 850 (CH_2), 762, 662 cm^{-1}; ^1H nmr (acetone-d_6): δ 0.46 (s, 9H, $(CH_3)_3$), 5.24 (m, 16H, OCH_2), 5.50-6.40 (br, 8H, OCH_2), 7.70-8.30 (br, 3H, H_{arom}); ms: fast-atom-bombardment m/z 1852.1 (M^+, 100), 1769.0 (M^+ - CF_3CH_2, 24.9), 1686.2 (M^+ - 2 x CF_3CH_2, 8.81); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 732.0 (5.33), 657.0 (4.64), 353.0 (4.84), 231.0 (5.01).

Anal. Calcd. for $C_{61}H_{36}N_8F_{36}O_{13}SiV$ (1851.97): C, 39.56; H, 1.96; N, 6.05; F, 36.93. Found: C, 39.59; H, 1.96; N, 6.06; F, 37.13.

Zinc 23-(3'-hydroxy-3'-methyl-1'-butynyl)-1,2,3,4,8,9,10,11,15,-16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**4b**).

Quantities: zinc 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (35 mg, 1.86 x 10^{-2} mmole), 3-methyl-1-butyn-3-ol (20 mg, 0.238 mmole), bis(triphenylphosphine)palladium dichloride (1.0 mg, 1.43 x 10^{-3} mmole), copper(I) iodide (1.0 mg, 5.25 x 10^{-3} mmole), anhydrous tetrahydrofuran (10 ml), and anhydrous triethylamine (10 ml); reaction conditions: 35-40°, 24 hours. The experimental procedure was as described for the preparation of compound **4a**. The crude product was purified by column chromatography on silica gel with 3:1, 2:1 and 1:1 (volume ratio) hexane/ethyl acetate as the first, second and third eluent to remove the yellow impurities, followed by eluting with dichloromethane/tetrahydrofuran (10:1, volume ratio) as an eluent to give a green fraction of **4b**. The crude unsymmetrical product was further purified by column chromatography on silica gel with hexane/ethyl acetate (1:2, volume ratio) as an eluent to give a green solid. Recrystallization from ethyl acetate-hexane (1:18) yielded a green microcrystalline solid, 31 mg

(90.6%); ir: ν_{max} 3090 (=CH), 2968, 2935, 2862 (CH_2), 2347 (ethynyl), 1718, 1674, 1634, 1613 (C=C ring), 1486 (C=C ring), 1454, 1432 (CH_2), 1406, 1273, 1245 (C-O), 1161 (C-F), 1123 (ring), 1068, 1008, 969 (C-O), 853 (CH_2), 751, 662 cm^{-1}; ^1H nmr (acetone-d_6): δ 1.45 (m, 6H, 2 x CH_3), 4.25 (s, 1H, OH), 5.18 (m, 12H, 6 x OCH_2), 5.74 (m, 8H, 4 x OCH_2), 5.99 (m, 4H, 2 x OCH_2), 7.71 (d, J = 8.50 Hz, 1H, H_{arom}), 8.22 (d, J = 8.50 Hz, 1H, H_{arom}), 9.30 (s, 1H, H_{arom}); ms: fast-atom-bombardment m/z 1834.2 (M^+ -1, 100), 1835.2 (M^+, 100, ^{64}Zn-**4b** requires M^+ 1834.93), 1836.2 (M^+ +1, 100), 1837.2 (M^+, 95.6, ^{66}Zn-**4b**), 1838.3 (M^+ +1/^{66}Zn-**4b**, M^+/^{67}Zn-**4b**, 92.9), 1839.2 (M^+, 59.3)/1840.2 (M^+ +1, 27.5)(^{68}Zn-**4b**), 1841.3 (M^+, 10.8, ^{70}Zn-**4b**); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 702.0 (5.30), 631.5 (4.58), 360.5 (4.79), 309.0 (4.58), 225.5 (4.99).

Anal. Calcd. for $C_{61}H_{34}N_8F_{36}O_{13}Zn$ (1836.32): C, 39.90; H, 1.87; N, 6.10; F, 37.25. Found: C, 40.44; H, 2.26; N, 5.66; F, 37.06.

Vanadyl 23-(2'-(4"-nitrophenyl)ethynyl)-1,2,3,4,8,9,10,-11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**5a**).

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (90 mg, 4.78 x 10^{-2} mmole), 4-nitrophenylacetylene (22 mg, 0.15 mmole), bis(triphenylphosphine)palladium dichloride (3.0 mg, 4.29 x 10^{-3} mmole), copper(I) iodide (2.0 mg, 1.05 x 10^{-2} mmole), anhydrous tetrahydrofuran (30 ml), and anhydrous triethylamine (30 ml); reaction conditions: 30-40°, 48 hours. The experimental procedure was as described for the preparation of compound **4a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent to give the second fraction of **5a**. The crude unsymmetrical product was further purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, volume ratio) as an eluent to give a dark green solid. Recrystallization from ethyl acetate-hexane (1:18, three times) yielded a dark green microcrystalline solid, 86.4 mg (95.0%); ir: ν_{max} 3070 (=CH), 2977 (CH_2), 2357 (ethynyl), 1636, 1624, 1616, 1593 (C=C ring), 1522 (NO_2), 1489 (C=C ring), 1456, 1429 (CH_2), 1339 (NO_2), 1275, 1248 (C-O), 1159 (C-F), 1115 (ring), 1067, 1011, 972 (C-O), 856 (CH_2), 750, 660 cm^{-1}; ^1H nmr (acetone-d_6): δ 5.29 (m, 16H, OCH_2), 5.60-6.50 (br, 8H, OCH_2), 8.00-8.90 (br, H_{arom}); ms: fast-atom-bombardment m/z 1901.0 (M^+, 100), 1818.0 (M^+ - CF_3CH_2, 33.4); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/dm^3mol^{-1} cm^{-1}] 733.0 (5.34), 658.0 (4.65), 350.0 (4.87), 226.0 (5.08).

Anal. Calcd. for $C_{64}H_{31}N_9F_{36}O_{15}V$ (1900.89): C, 40.44; H, 1.64; N, 6.63; F, 35.98. Found: C, 40.61; H, 1.67; N, 6.59; F, 36.16.

Zinc 23-(2'-(4"-nitrophenyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,-17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**5b**).

Quantities: zinc 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (140 mg, 7.45 x 10^{-2} mmole), 4-nitrophenylacetylene (33 mg, 0.224 mmole), bis(triphenylphosphine)palladium dichloride (4.0 mg, 5.70 x 10^{-3} mmole), copper(I) iodide (2.0 mg, 1.05 x 10^{-2} mmole), anhydrous tetrahydrofuran (30 ml), and anhydrous triethylamine (30 ml); reaction conditions: 25-30°, 24 hours. The experimental procedure was as described for the preparation of compound **4a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (1:1 to 1:2, volume ratio) as an eluent to give a green fraction of **5b**. The crude unsymmetrical product was further purified by column chromatography on silica gel with chloroform/tetrahydrofuran (100:1 to 25:1, volume ratio) as an eluent to give a dark green solid. Recrystallization from ethyl acetate-hexane (1:18, twice) yielded a dark green microcrystalline solid, 130 mg (92.2%); ir: ν_{max} 3020 (=CH), 2968, 2928, 2857 (CH_2), 2210 (ethynyl), 1629, 1610, 1594 (C=C ring), 1518 (NO_2), 1486 (C=C ring), 1452, 1431 (CH_2), 1406, 1342 (NO_2), 1274, 1246 (C-O), 1159 (C-F), 1111 (ring), 1068, 1008, 970 (C-O), 855 (CH_2), 750, 661 cm^{-1}; ^1H nmr (acetone-d_6): δ 5.17 (m, 12H, 6 x OCH_2), 5.49 (m, 4H, 2 x OCH_2), 5.66 (m, 4H, 2 x OCH_2), 6.29 (m, 4H, 2 x OCH_2), 7.80 (d, J_1 = 8.24 Hz, 2H, H_{arom}), 8.20 (d, J_1 = 8.24 Hz, 2H, H_{arom}), 8.30 (d, J_2 = 7.91 Hz, 1H, H_{arom}), 9.17 (d, J_2 = 7.91 Hz, 1H, H_{arom}), 9.25 (s, 1H, H_{arom}); ms: fast-atom-bombardment m/z 1896.9 (M^+ -1, 99.4), 1897.9 (M^+, 100, ^{64}Zn-**5b** requires M^+ 1897.94), 1898.9 (M^+ +1, 100), 1899.9 (M^+, 90.8, ^{66}Zn-**5b**), 1900.9 (M^+ +1/^{66}Zn-**5b**, M^+/^{67}Zn-**5b**, 89.1), 1901.8 (M^+, 59.9)/1902.9 (M^+ +1, 35.1)(^{68}Zn-**5b**), 1903.9 (M^+, 16.4, ^{70}Zn-**5b**); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 704.0 (5.43), 633.5 (4.71), 358.0 (4.93), 222.0 (5.07).

Anal. Calcd. for $C_{64}H_{31}N_9F_{36}O_{14}Zn$ (1899.33): C, 40.47; H, 1.65; N, 6.64; F, 36.01. Found: C, 40.98; H, 1.99; N, 6.27; F, 35.47.

Vanadyl 23-(2'-(4"-aminophenyl)ethynyl)-1,2,3,4,8,9,10,11,-15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**5c**).

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (100 mg, 5.31 x 10^{-2} mmole), 4-aminophenylacetylene (18 mg, 0.154 mmole), bis(triphenylphosphine)palladium dichloride (3.0 mg, 4.28 x 10^{-3} mmole), copper(I) iodide (1.5 mg, 7.88 x 10^{-3} mmole), anhydrous tetrahydrofuran (30 ml), and anhydrous triethylamine (30 ml); reaction conditions: room temperature, 48 hours. The experimental procedure was as described for the preparation of compound **4a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent (twice) to give a dark purple solid. Recrystallization from ethyl acetate-hexane (1:18, three times) yielded a dark purple microcrystalline solid, 74.6 mg (75.1%); ir: ν_{max} 3229 (NH_2), 3080 (=CH), 2969, 2928, 2863 (CH_2), 2201 (ethynyl), 1627, 1602 (C=C ring), 1519, 1488 (C=C ring), 1452, 1429 (CH_2), 1276, 1246 (C-O), 1160 (C-F), 1113 (ring), 1067, 1010, 972 (C-O), 852 (CH_2), 833, 760, 662 cm^{-1}; ^1H nmr (acetone-d_6): δ 4.25 (m, NH_2), 5.28 (m, 16H, OCH_2), 5.60-7.00 (br, 8H, OCH_2), 7.20-8.30 (br, H_{arom}); ms: fast-atom-bombardment m/z 1871.2 (M^+, 100), 1788.2 (M^+ - CF_3CH_2, 26.5); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 740.0 (5.29), 664.5 (4.64), 354.0 (4.93), 265.5 (4.70), 229.0 (4.99).

Anal. Calcd. for $C_{64}H_{33}N_9F_{36}O_{13}V$ (1870.90): C, 41.09; H, 1.78; N, 6.74; F, 36.58. Found: C, 41.58; H, 1.89; N, 6.62; F, 37.16.

Vanadyl 23-(2'-(4"-formylphenyl)ethynyl)-1,2,3,4,8,9,10,11,15,-16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**5d**).

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (60 mg, 3.19 x 10^{-2} mmole), freshly prepared 4-formyl-phenylacetylene

(12 mg, 9.23 x 10^{-2} mmole), bis(triphenylphosphine)palladium dichloride (3.0 mg, 4.29 x 10^{-3} mmole), copper(I) iodide (2.0 mg, 1.05 x 10^{-2} mmole), anhydrous tetrahydrofuran (20 ml), and anhydrous triethylamine (20 ml); reaction conditions: 30-40°, 24 hours. The experimental procedure was as described for the preparation of compound **4a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent (twice) to give a green solid. Recrystallization from ethyl acetate - hexane (1:18, three times) yielded a green microcrystalline solid, 48 mg (80.0%); ir: ν_{max} 3070 (=CH), 2971, 2928, 2857 (CH_2), 2210 (ethynyl), 1700 (CHO), 1633, 1612, 1600 (C=C ring), 1563, 1488 (C=C ring), 1454, 1429 (CH_2), 1275, 1247 (C-O), 1159 (C-F), 1113 (ring), 1067, 1010, 972 (C-O), 854 (CH_2), 834, 760, 662 cm^{-1}; ^1H nmr (acetone-d_6): δ 5.31 (m, 16H, OCH_2), 5.60-6.80 (br, 8H, OCH_2), 7.20-8.50 (br, H_{arom}), 10.0 (m, CHO); ms: fast-atom-bombardment m/z 1884.9 (M^+ + 1, 97.3), 1883.9 (M^+, 100), 1882.9 (M^+ - 1, 100), 1800.9 (M^+ - CF_3CH_2, 42.8), 1817.9 (M^+ - 2 x CF_3CH_2, 13.6); uv/visible (1,4-dioxane): λ_{max}/nm [log ε/$dm^3mol^{-1}cm^{-1}$] 733.5 (5.31), 658.5 (4.61), 354.0 (4.83), 326.5 (4.79), 229.0 (4.99).

Anal. Calcd. for $C_{65}H_{32}N_8F_{36}O_{14}V$ (1883.90): C, 41.44; H, 1.71; N, 5.95; F, 36.30. Found: C, 41.91; H, 1.77; N, 5.85; F, 36.16.

REFERENCES AND NOTES

* To whom correspondence should be addressed.

† Present address: Corporate Research Center, Fuji Xerox Co., Ltd., 430 Sakai, Nakai-machi, Ashigarakami-gun, Kanagawa 259-0157, Japan

[1a] F. H. Moser and A. L. Thomas, Phthalocyanine Compounds, Reinhold, New York; Chapman and Hall, London, 1963; [b] F. H. Moser and A. L. Thomas, The Phthalocyanines, Vols **I** and **I I**, CRC Press, Boca Raton, Florida, 1983.

[2] C. C. Leznoff and A. B. P. Lever, eds, Phthalocyanines, Properties and Applications, Vols **1**, **2**, **3** and **4**, VCH Publishers, Inc, Weinheim, New York, 1989, 1993, 1993, 1996.

[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] N. B. McKeown, I. Chambrier and M. J. Cook, *J. Chem. Soc., Perkin Trans. 1*, 1169 (1990); [d] 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); [e] M. J. Cook, G. Cooke and A. Jafari-Fini, *J. Chem. Soc., Chem. Commun.*, 1715 (1995); [f] G. J. Clarkson, N. B. McKown and K. E. Treacher, *J. Chem. Soc., Perkin Trans. 1*, 1817 (1995); [g] G. C. Bryant, M. J. Cook, T. G. Ryan and A. J. Thorne, *Tetrahedron*, **52**, 809 (1996); [h] G. J. Clarkson, A. Cook, N. B. McKeown, K. E. Treacher and Z. Ali-Adib, *Macromolecules*, **29**, 913 (1996); [i] G. J. Clarkson, B. M. Hassan, D. R. Maloney and N. B. McKeown, *Macromolecules*, **29**, 1854 (1996).

[5a] 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, 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).

[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] 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); [d] A. Sastre, B. del Rey and T. Torres, *J. Org. Chem.*, **61**, 8591 (1996).

[8a] M. Kimura, T. Dakeno, E. Adachi, T. Koyama, K. Hanabusa and H. Shirai, *Macromol. Chem. Phys.*, **195**, 2423 (1994); [b] H. Ali and J. E. van Lier, *Tetrahedron Letters*, **38**, 1157 (1997); [c] A. Hirth, A. K. Sobbi and D. Wöhrle, *J. Porphyrins Phthalocyanines*, **1**, 275 (1997).

[9a] 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 and Y. Qin, *Can. J. Chem.*, **71**, 1319 (1993); [g] J. Vacus, G. Memetzidis, 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. Linßen 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); [m] M. Aoudia, G. Cheng, V. O. Kennedy, M. E. Kenney and M. A. J. Rodgers, *J. Am. Chem. Soc.*, **119**, 6029 (1997); [n] R. Polley, T. G. Linßen, P. Stihler and M. Hanack, *J. Porphyrins Phthalocyanines*, **1**, 169 (1997); [o] G. de la Torre and T. Torres, *J. Porphyrins Phthalocyanines*, **1**, 221 (1997); [p] X. Ding, S. Shen, Q. Zhou and H. Xu, *Dyes and Pigments*, **40**, 187 (1999); [q] S. Makhseed, A. Cook and N. B. McKeown, *Chem. Commun.*, 419 (1999).

[10a] 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).

[11a] 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 and 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); [h] S. V. Kudrevich, S. Gilbert and J. E. van Lier, *J. Org. Chem.*, **61**, 5706 (1996).

[12] B. Cabezón, S. Rodríguez-Morgade and T. Torres, *J. Org. Chem.*, **60**, 1872 (1995).

[13] J. G. Young and Onyebuagu, *J. Org. Chem.*, **60**, 1872 (1995).

[14] K. Sonogashira, in Comprehensive Organic Synthesis, Vol **3**, B. M. Trost and I. Fleming, eds, Pergamon Press, Oxford, 1991, p 521.

[15a] M. Tian, T. Wada, H. Kimura and H. Sasabe, *Mol. Cryst. Liq. Cryst.*, **294**, 271 (1997); [b] M. Tian, T. Wada, H. Kimura-Suda and H. Sasabe, *J. Mater. Chem.*, **7**, 861 (1997).

[16a] J . L. Brédas, C. Adant, P. Tackx and A. Persoons, *Chem. Rev.*, **94**, 243 (1994); [b] N. J. Long, *Angew. Chem. Int. Ed. Engl.*, **34**, 21 (1995); [c] H. S. Nalwa and J. S. Shirk, in Phthalocyanines, Properties and Applications, Vol **4**, C. C. Leznoff and A. B. P. Lever, eds, VCH Publishers, Inc., New York, 1996, pp 79-181 and refs. therein.

[17] S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 627 (1980).

[18] W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, **46**, 2280 (1981).

[19a] H. A. Tayim, A. Bouldoukian and F. Award, *J. Inorg. Nucl. Chem.*, **32**, 3799 (1970); [b] H. Itatani and J. C. Bailar, *J. Am. Oil Chem. Soc.*, **44**, 147 (1967).

[20] M. Tian, T. Wada and H. Sasabe, *J. Heterocyclic Chem.*, **34**, 171 (1997).

[21] 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 290-295.

[22] W. Eberhardt and M. Hanack, *Synthesis*, 95 (1997).

[23] S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever, C. C. Leznoff and K. B. Tomer, *Can. J. Chem.*, **63**, 3057 (1985).

[24] P. J. Brach, S. J. Grammatica, O. A. Ossanna and L. Weinberger, *J. Heterocyclic Chem.*, **7**, 1403 (1970).

[25a] R. W. Boyle, C. K. Johnson and D. Dolphin, *J. Chem. Soc., Chem. Commun.*, 527 (1995); [b] S. M. LeCours, H. W. Guan, S. G. DiMagno, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, **118**, 1497 (1996).

[26] K.-Y. Law, *Inorg. Chem.*, **24**, 1778 (1985).

[27] M. Gouterman, The Porphyrins, Vol **III**, D. Dolphin, ed, Academic Press, New York, 1978, pp 1-165.