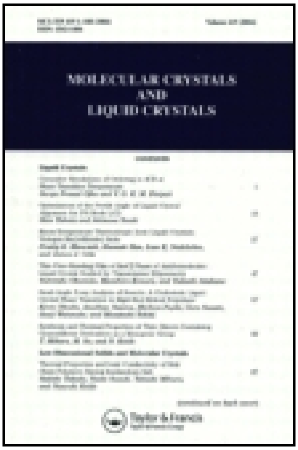

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Novel Asymmetrically Substituted Metallophthalocyanines for Nonlinear Optics

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NOVEL ASYMMETRICALLY SUBSTITUTED METALLOPHTHALOCYANINES FOR NONLINEAR OPTICS

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Abstract Highly soluble asymmetrically substituted vanadylphthalocyanines with dodecakis(2,2,2-trifluoroethoxy) groups as a donor and a mono-nitro group as an acceptor substituent, or with extended exocyclic conjugation, have been synthesized and characterized. Their linear and nonlinear optical properties were studied. Second harmonic generation of thin films of poly(methyl methacrylate) doped with these vanadylphthalocyanines was observed after electric poling at a fundamental wavelength of 1.064 μm.

INTRODUCTION

Phthalocyanines are an important class of third-order nonlinear optical materials.[1,2] The attractive and outstanding characteristics of phthalocyanines are their two-dimensional π-electron conjugation, great structural variety, high thermal and chemical stability, film-forming properties. These properties also strongly depend on the peripheral and axial substitution patterns.[2,3,4] Up to now, a variety of symmetrical or pseudo-symmetrical tetra-, octa- and hexadeca-substituted phthalocyanines have been reported.[3,4] Recently, asymmetrical phthalocyanines have attracted a lot of interest in the field of second-order nonlinear optics,[5] liquid crystals,[6] Langmuir-Blodgett (LB) films[7] and photodynamic therapy of cancer.[8] They are also very important in understanding the nature of phthalocyanine molecules. Nevertheless, there have been only a limited number of reports on asymmetrical phthalocyanines because of their preparative difficulty.

Previously, we have reported the synthesis and second-order nonlinear optical properties of an unsymmetrical phthalocyanine with a mono-nitro group as an acceptor substituent and three *tert*-butyl groups as a donor substituent.[5,9] In order to search for new materials for second-order nonlinear optics, we are interested in asymmetrical phthalocyanines with conjugated donor-acceptor system. In this paper, we report the synthesis, spectroscopic, and second-order nonlinear optical properties of some novel asymmetrically substituted metallophthalocyanines (See Figure 1).

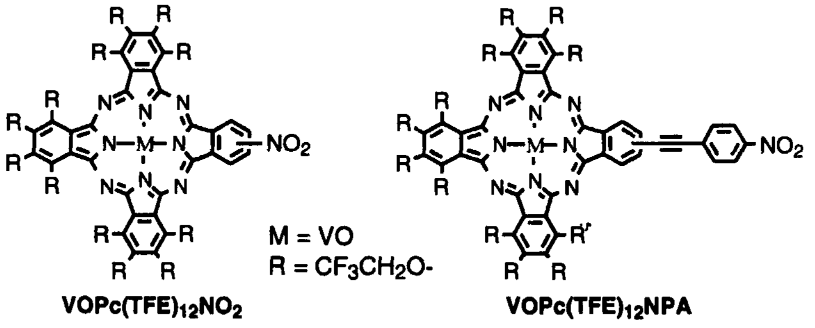
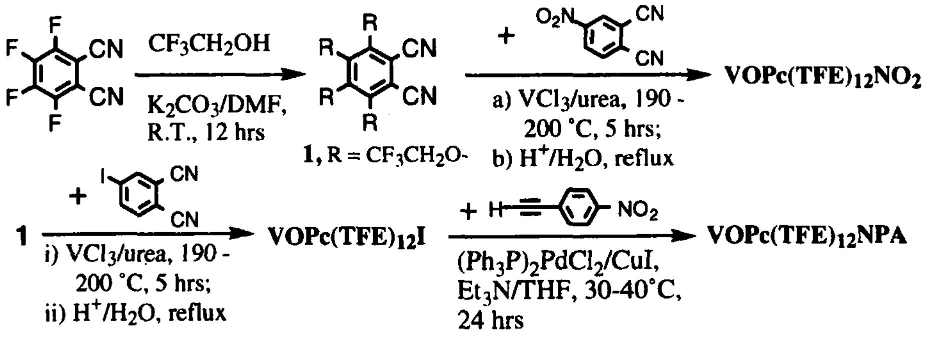


FIGURE 1. Molecular structures of new asymmetrical metallophthalocyanines for NLO.

EXPERIMENTAL

The target materials 23-nitro- and 23-(2-(4-nitrophenyl)ethynyl)- 1,2,3,4,8,9,10,11, 15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl complexes, VOPc(TFE)$_{12}$NO$_2$ and VOPc(TFE)$_{12}$NPA, were synthesized according to Scheme 1.



SCHEME 1 Syntheses of new asymmetrical metallophthalocyanines for NLO.

Compound **1** was prepared by a modification of the reference method[10] in 94.5% yield. The mixed condensation of a 1:5 molar ratio of **1** and 4-nitrophthalonitrile in the presence of an excess of VCl$_3$ and dry urea at 190-200 °C yielded a black-green solid. The solid was refluxed with 5% HCl acid, then filtered, washed with water, and dried to give a crude product. Multiple column chromatography on silica gel was carried out to obtain VOPc(TFE)$_{12}$NO$_2$ as a dark green solid. Yield 16.3%.

Similarly, vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (VOPc(TFE)$_{12}$I) was prepared by the mixed condensation of a 1:3 molar ratio of **1** and 4-iodophthalonitrile[11] in 23% yield. The coupling reaction between VOPc(TFE)$_{12}$I and an excess of 4-nitrophenylacetylene in Et$_3$N/THF (1:1) with

$(Ph_3P)_2PdCl_2$ and CuI as catalysts at 30-40 °C under dry N_2 gave VOPc(TFE)$_{12}$NPA as a dark green solid after purification. Yield 94.5%.

The chemical structures of VOPc(TFE)$_{12}$$NO_2$ and VOPc(TFE)$_{12}$NPA were confirmed by the results of FT-IR, ^{1}H-NMR, FAB-Mass, UV-Visible spectroscopies and elemental analysis.

RESULTS AND DISCUSSION

The UV-visible absorption spectra of two asymmetrically substituted vanadylphthalocyanines are shown in Figure 2. The absorption spectrum of VOPc(TFE)$_{12}$NPA is quite similar to that of VOPc(TFE)$_{12}$$NO_2$, however, a red-shifted absorption peak of Q-band was observed, due to the extended exocyclic π-conjugation.

Figure 3 shows the typical SHG Maker fringe result of thin films of poly(methyl methacrylate) (PMMA) doped with VOPc(TFE)$_{12}$$NO_2$ or VOPc(TFE)$_{12}$NPA on glass substrate after electric poling. Under the same condition of thickness and concentration, VOPc(TFE)$_{12}$NPA films showed larger second-harmonic signals than those of VOPc(TFE)$_{12}$$NO_2$, which can be attributed to the enhanced molecular second-order nonlinearity in the molecules with extended exocyclic π-conjugation.

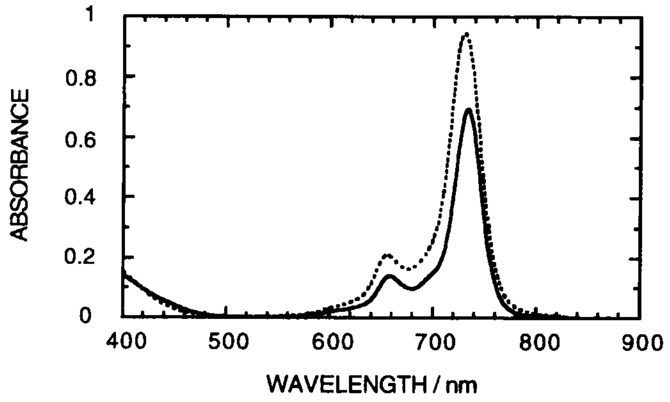


FIGURE 2 UV-visible absorption spectra of VOPc(TFE)$_{12}$$NO_2$ (broken line) and VOPc(TFE)$_{12}$NPA (solid line) in 1,4-dioxane.

CONCLUSIONS

Two novel soluble asymmetrically substituted vanadylphthalocyanines with donor and acceptor groups have been successfully synthesized and fully characterized. The asymmetrical phthalocyanine with extended exocyclic π-conjugation shows a red-shift of the Q-band absorption peak and an enhanced second-order nonlinear susceptibility. These

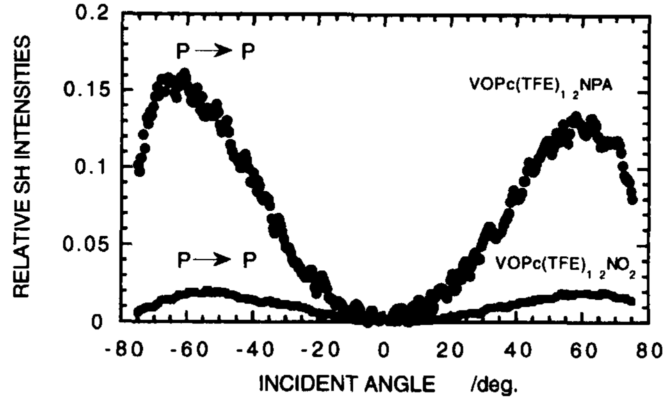


FIGURE 3 SHG Maker fringe data of VOPc(TFE)$_{12}$NO$_2$ and VOPc(TFE)$_{12}$NPA (doped in PMMA, 5%wt, thickness 1.5 μm) on glass substrate at 1.064 μm.

asymmetrically substituted phthalocyanines can be applied as thermally stable second-order nonlinear optical chromophores.

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