MATERIALS CHEMISTRY COMMUNICATION

Novel non-aggregated unsymmetrical metallophthalocyanines for second-order non-linear optics

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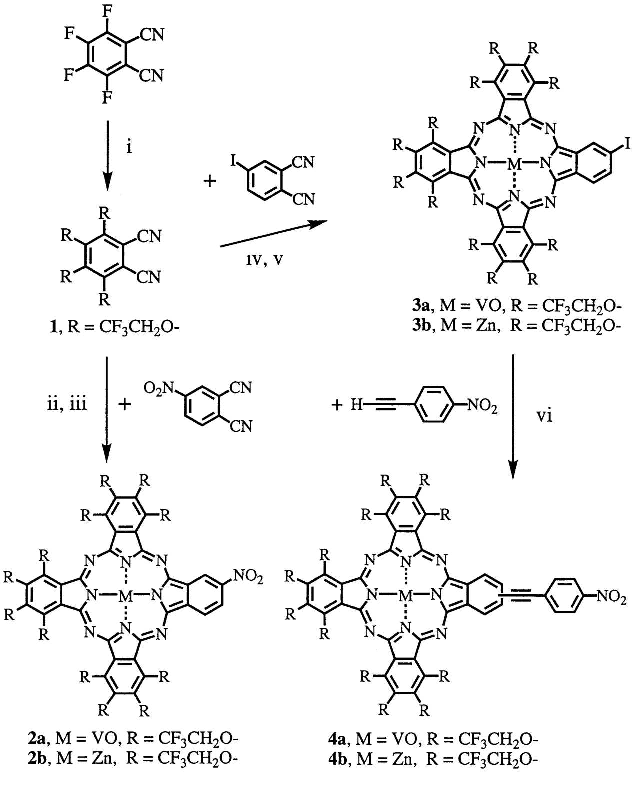
Novel soluble unsymmetrical metallophthalocyanines with twelve 2,2,2-trifluoroethoxy groups as donor substituents and a mono-nitro or an exocyclic conjugated nitro group as an acceptor substituent have been synthesized and characterized. A study of the concentration dependence of UV–VIS absorption spectra showed they were non-aggregated phthalocyanines in solution and in doped polymer films. Second harmonic generation of spin-coated thin films of poly(methyl methacrylate) doped with these metallophthalocyanines was observed after electric poling at 110 °C for 30 min at a fundamental wavelength of 1.064 μm.

Phthalocyanines (Pcs) have attracted great research attention for many years because of their two-dimensional π-electron conjugation, great structural variety, high thermal and chemical stability, and unique electrical, optical, magnetic, catalytic, mesogenic and film-formation properties for various applications.[1–3] Up to now, a variety of symmetrical or pseudo-symmetrical tetra-, octa- and hexadeca-substituted phthalocyanines have been reported.[1–4] However, there have been only a limited number of reports on unsymmetrical phthalocyanines because of their preparative difficulty.[5] In the last decade, the third-order non-linear optical (NLO) properties of phthalocyanines have been well studied.[6] Although it has been pointed out that unsymmetrical phthalocyanines with donor and acceptor groups should possess second-order NLO properties,[7] there have been few reports on this research subject. In our previous study, we reported the synthesis and second-order NLO properties of a Langmuir–Blodgett film of an unsymmetrical phthalocyanine with a nitro group as an acceptor substituent and three *tert*-butyl groups as donor substituents.[8,9] On the other hand, mononuclear species of phthalocyanines usually show intermolecular aggregation in common organic solvents at high concentrations and in the solid state.[10] We found the molecular aggregation effect has an important influence on the linear and third-order NLO properties of metallophthalocyanines.[11] In order to study the influence of molecular aggregation on the second-order NLO properties of unsymmetrical phthalocyanines in the condensed state, we are interested in non-aggregated unsymmetrical phthalocyanines with conjugated donor–acceptor systems. Here we report the results of syntheses, spectroscopic, and second-order NLO properties of some novel unsymmetrically substituted metallophthalocyanines (see Scheme 1, compounds **2a**, **2b**, **4a** and **4b**) which suppress molecular aggregation even in the solid state.



Scheme 1 *Reagents and conditions*: i, CF_3CH_2OH, K_2CO_3–DMF, room temp., 12 h, 94.5%; ii, VCl_3 (or $ZnCl_2$), urea, 180–200 °C, 2–5 h; iii, H^+–water, reflux, 2–4 h; iv, VCl_3 (or $ZnCl_2$), urea, 180–200 °C, 2–5 h; v, H^+–water, reflux, 2–4 h; vi, $(Ph_3P)_2PdCl_2$–CuI, Et_3N–THF, 30–40 °C, 24 h, 85–95%

The target materials are unsymmetrically dodecakis(2,2,2-trifluoroethoxy)-substituted metallophthalocyanines with a nitro or 4-nitrophenylethynyl group on one of the benzene units. 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 interaction. Secondly, twelve trifluoroethoxy groups may also be expected to serve as donor groups, and a nitro group as an acceptor substituent. Thus the target phthalocyanines are two-dimensional conjugated systems containing both donor and acceptor. We expect that the extended exocyclic conjugation in **4a** and **4b** may enhance the molecular second-order non-linearity. The different central metal parts are also of interest because the NLO properties of phthalocyanines depend strongly on the peripheral and axial substitution patterns.[6] Moreover, the target unsymmetrical phthalocyanines not only can be expected to have second-order NLO properties but also are third-order NLO materials because of their two-dimensional π-conjugated structures. Finally, we expect that the target unsymmetrical phthalocyanines may be thermally stable candidates for poled-polymer applications.

The syntheses of the target materials are shown in Scheme 1. 3,4,5,6-Tetrakis(2,2,2-trifluoroethoxy)phthalonitrile **1** was prepared by a modification of the published method.[4,12] 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 h gave **1** in 94.5% yield. The statistical condensation of a 1 : 5 molar ratio of **1** and 4-nitrophthalonitrile in the presence of an excess of metal salt and dry urea at 180–200 °C produced the desired unsymmetrical metallophthalocyanines **2a** and **2b** in 16.3% and 15.0% yield, respectively.

Similarly, the new unsymmetrical monoiodinated phthalocyanines **3a** and **3b** were synthesized by the mixed condensation of a 1 : 3 molar ratio of **1** and 4-iodophthalonitrile[13] in 23% and 16% yield, respectively. The cross-coupling reaction between monoiodinated metallophthalocyanines **3a**, **b** and an excess of 4-nitrophenylacetylene[14] in triethylamine–tetrahydrofuran (1 : 1) with bis(triphenylphosphine)palladium chloride and copper(I) iodide as catalyst at 30–40 °C under a dry nitrogen atmosphere gave compounds **4a** and **4b** as dark green solids in high yields after purification.

All the new unsymmetrical phthalocyanines **2**–**4** were purified by column chromatography on silica gel with hexane–ethyl acetate (vol. ratio 4 : 1 for **3a**, 3 : 1 for **2a**, **3b** and **4a**, 3 : 1 to 1 : 1 for **2b** and **4b**) several times and then recrystallized from ethyl acetate–hexane. Their structures were identified by UV–VIS, FAB-MS, IR and ^{1}H NMR spectroscopic methods, as well as by elemental analysis.† In the UV–VIS absorption spectra of **2a**, **2b**, **4a** and **4b** in 1,4-dioxane, there is a transparent window region between 480 and 580 nm, which is very useful for second harmonic generation research. However, despite the extension of exocyclic conjugation from **2** to **4**, no obvious red-shift of the Q-band was observed in the UV–VIS absorption spectra. This may be explained by the reduction of effective conjugation between the phthalocyanine ring and the exocyclic phenyl ring owing to the rotation of benzene ring around the carbon–carbon triple bond.

All the new compounds **2**–**4** show very good solubility in polar organic solvents like diethyl ether, tetrahydrofuran, ethyl acetate and acetone. The thermal stability of the target unsymmetrical phthalocyanines was studied by thermogravimetry (TG). For example, the initial decomposition temperature, flection temperature and maximum decomposition temperature for **2a** are 313.8, 343.1 and 388.8 °C, while for **4a** they are 178.7, 381.5 and 408.4 °C, respectively. These results indicate that the target materials are sufficiently thermally stable for some poled-polymer applications.

Fig. 1 shows the absorption spectra for spin-coated poly(methyl methacrylate) (PMMA) films doped with various concentrations of **2a** normalized by the peak value. Mononuclear phthalocyanine generally shows no sign of intermolecular aggregation in common solvents at concentrations below 1×10^{-5} M at room temperature.[10] At higher concentrations, however, intermolecular aggregation can occur. In Fig. 1, the concentration in chloroform solution of **2a** is $<1\times10^{-5}$ M and then the spectrum for chloroform solution represents the non-aggregated or 'monomeric' state. For **2a**, the Q-band absorption position does not change with the concentration of doped phthalocyanine. Besides, no significant blue-shift of the Q-band was observed from the comparison of the absorption spectra in chloroform solution and in the solid state. These phenomena are contrary to those of aggregated phthalocyanines in the condensed state, such as tetrakis(*tert*-butyl) metal-free phthalocyanine.[15] These results can be explained from the dodecakis(2,2,2-trifluoroethoxy) substitution of the phthalocyanine ring. The strong repulsive effect between electronegative fluorine atoms reduces the possibility of severe aggregation between phthalocyanine molecules in the solid state. The aggregation properties of **2b**, **4a** and **4b** in the solid state were similar to that of **2a**. Therefore, the target compounds **2a**, **2b**, **4a** and **4b** can be considered to be non-aggregated metallophthalocyanines.

Thin films of PMMA doped with the target unsymmetrical phthalocyanines **2** and **4** with a thickness of *ca.* 1.5 µm were obtained on a glass substrate by a spin coating method from

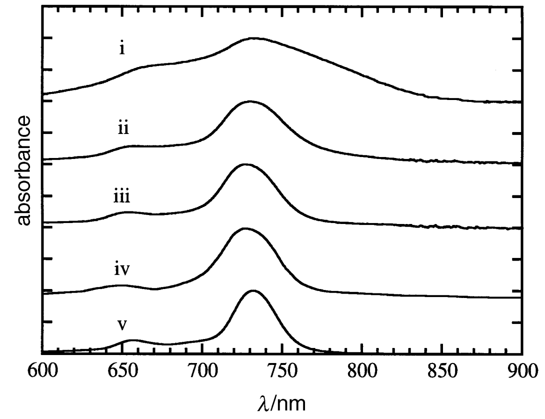


Fig. 1 UV–VIS absorption spectra of **2a** in solution and in doped PMMA films: i, neat film without polymer; ii, with a concentration of 10 mass%; iii, with a concentration of 1 mass%; iv, with a concentration of 0.1 mass%; v, in chloroform solution

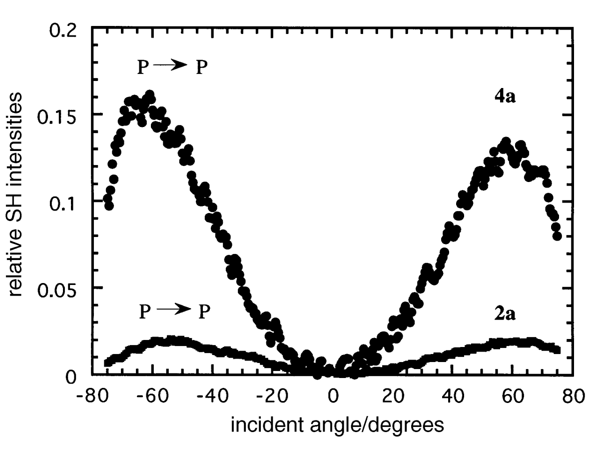


Fig. 2 SHG Maker fringe data of poled films of **2a** and **4a** (doped in PMMA, 5 mass%, film thickness 1.5 µm) on a glass substrate at 1.064 µm

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† Selected spectroscopic data for **3b**: ^{1}H NMR (270 MHz, CD_3COCD_3) δ 5.18 (m, 12H, $6\times OCH_2$), 5.65 (m, 4H, $2\times OCH_2$), 5.80 (q, 4H, $J=8.58$ Hz, $2\times OCH_2$), 5.96 (q, 4H, $J=8.58$ Hz, $2\times OCH_2$), 8.33 (d, 1H, $J=8.50$ Hz, H_{arom}), 8.75 (d, 1H, $J=8.50$ Hz, H_{arom}), 9.25 (s, 1H, H_{arom}); FAB-MS (*m*-NBA) *m/z* 1877.9 (M^+-1, 100.0%), 1878.8 (M^+, 87.60, ^{64}Zn-**3b** requires M^+ 1878.72), 1879.8 (M^++1, 92.04), 1880.8 (M^+, 70.46, ^{66}Zn-**3b**), 1881.8 ($M^++1/^{66}$Zn-**3b**, $M^+/^{67}$Zn-**3b**, 70.15), 1882.8 (M^+, 37.67), 1883.8 (M^++1, 20.12) (^{68}Zn-**3b**), 1884.8 (M^+, 7.97)(^{70}Zn-**3b**). For **2a**: ^{1}H NMR (270 MHz, CD_3COCD_3) δ 5.28 (m, 12H, $6\times OCH_2$), 5.50–6.50 (br m, 12H, $6\times OCH_2$), 9.30–9.80 (br, H_{arom}); FAB-MS (*m*-NBA) *m/z* 1800.9 (M^+, 100.0%, requires M^+ 1800.77), 1718.0 ($M^+-CF_3CH_2$, 25.4); UV–VIS λ_{max}(1,4-dioxane)/nm ($\log[\varepsilon/dm^3mol^{-1}cm^{-1}]$) 730.0 (5.23), 655.5 (4.58), 347.0 (4.76), 267.0 (4.52), 234.0 (4.73). For **4a**: yield 95.0%. ^{1}H NMR (270 MHz, CD_3COCD_3) δ 5.29 (m, 12H, $6\times OCH_2$), 5.60–6.50 (br, 12H, $6\times OCH_2$), 8.00–8.90 (br, H_{arom}); FAB-MS (*m*-NBA) *m/z* 1901.0 (M^+, 100.0%, requires M^+ 1900.89), 1818.0 ($M^+-CF_3CH_2$, 33.4); UV–VIS λ_{max} (1,4-dioxane)/nm ($\log[\varepsilon/dm^3mol^{-1}cm^{-1}]$) 733.0 (5.34), 658.0 (4.65), 350.0 (4.87), 226.0 (5.08).

their ethyl acetate solutions filtered through a 0.2 μm syringe filter, and then dried under high vacuum for 48 h. The orientation of the chromophores in the polymeric thin films was achieved by corona poling at 110 °C for 30 min with an applied dc electric field of 13.5 kV cm^{-1} between a tungsten wire electrode and the glass substrate, and subsequently monitored by the second harmonic generation (SHG). The SHG measurements were performed using a polarized Q-switched Nd–YAG laser beam ($\lambda = 1064$ nm). A Y-cut quartz crystal plate (second harmonic coefficient $d_{11} = 0.5$ pm V^{-1}) was used as the reference. The SHG intensity of the target materials was measured using the standard Maker fringe technique.[16] Fig. 2 shows the typical SHG Maker fringe results of poled thin films of PMMA doped with **2a** and **4a** on a glass substrate at a fundamental wavelength of 1.064 μm. The success in the observation of SHG of **2a** and **4a** demonstrates that non-aggregated metallophthalocyanines can be well poled under an electric field even in the condensed state. Under the same conditions of thickness and concentration (5 mass%), thin films of **4a** showed larger second-harmonic signals than those of **2a**, which may be attributed to the enhancement of the first-order hyperpolarizability (β) in the molecules of phthalocyanine **4a** with extended exocyclic π-conjugation. On the other hand, under the same poling condition, symmetrical hexadecakis(2,2,2-trifluoroethoxy)vanadylphthalocyanine [$VOPc(TFE)_{16}$] showed no SHG response. This result indicated that the observed SHG arose not from an electric-field-induced second-harmonic (EFISH) generation-like $\gamma(-2\omega; \omega, \omega, 0)$ value,[6b] but from a non-zero β term. To the best of our knowledge, no previous results on electric-field-induced alignment of unsymmetrical phthalocyanines doped in polymer films have been reported. A detailed study on the second-order NLO properties of these non-aggregated phthalocyanines is now in progress.

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