Enhanced Third-order Optical Nonlinearity in Helical Assembly of a Chiral Vanadyl Phthalocyanine

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A chiral vanadyl phthalocyanine formed helical aggregates with a left-handed helix sense; the aggregates showed an efficient third harmonic generation in as-prepared films and the $\chi^{(3)}$ value was enhanced by the chiral aggregation with reference to a mixture of racemic diastereoisomers.

Helical assembly of disk-shaped molecules is an attractive phenomenon in the fields of the molecular science.[1] Chiral phthalocyanine derivatives are one of the well-established planar molecules because of their strong tendency to form 1-D columnar aggregates.[2] Usually, the columnar stacks undergo large blue shifting and broadening for their Q-bands located around the visible region.[3] Conversely, the aggregation of nonplanar phthalocyaines develops the near-infrared (NIR) absorbing phase, e.g. phase II crystals,[4] induced by post treatments after deposition and this was considered to show good photoconductivity[5] and large nonlinear optical (NLO) properties.[6] Among them, vanadyl phthalocyanine shows efficient third-order nonlinear responses such as optical limiting responses.[7] Accordingly, we planned to designate chiral vanadyl phthalocyanine to the application for the chiral NLO materials, and synthesized a phthalocyanine derivative **1**. A thin film (spin-coating and cast) of this molecule exhibits unique Q-bands with an absorption maximum around 830 nm without any treatments after deposition. From this observation, we supposed that the aggregates of **1** are desirable for chiral optical applications especially for the NLO applications related to the NIR absorbing phases. In the present letter, we report a spontaneous formation of chiral aggregates from **1** molecules and the enhanced third-order NLO responses of the helical assembly. A vanadyl phthalocyanine **1** used in this study was prepared by heating of 4,5-di[(*S*)-2-methylbutoxy]phthalonitrile to 150 °C under the presence of VCl₃ and urea.
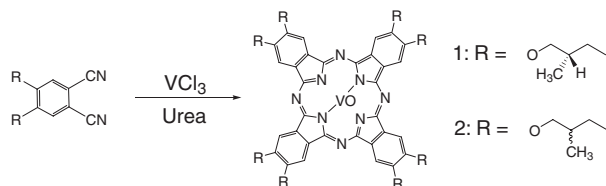
The analytical data of **1** are as expected.[8] Similarly, a mixture of racemic diastereoisomers, compound **2**, was prepared from 4,5-di[(*R*,*S*)-2-methylbutoxy]phthalonitrile. Figure 1 shows electronic absorption spectra of **1** in the mixture of CHCl₃ and MeOH with various mixed ratio. Phthalocyanine **1** exhibits sharp and intense Q-bands typical of monomeric vanadyl phthalocyanines in CHCl₃.[9] In contrast, the Q-bands of the mixed solvent system undergo a split relative to the CHCl₃ solution with increasing of a poor solvent such as MeOH. Notably, the grow-
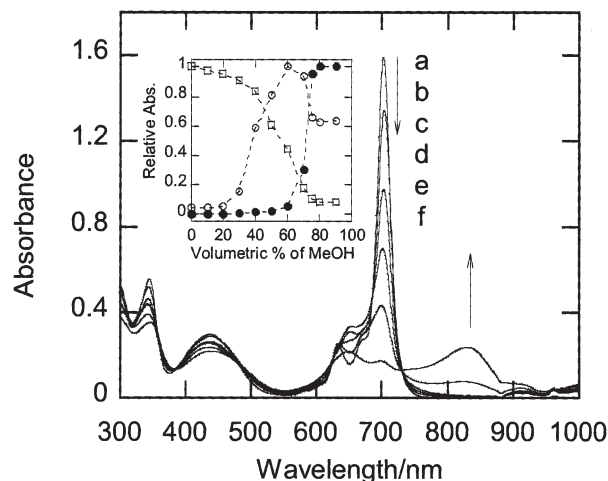

Figure 1. Absorption spectra of **1** ([**1**] = 7.9×10^{-6} mol dm⁻³) in the mixture of CHCl₃ and MeOH with vol % of MeOH (a) 0; (b) 40; (c) 50; (d) 60; (e) 70; (f) 80 vol %. The inset shows relative absorbance change at 702 (□), 650 (○), 830 nm (●).

ing of the two new bands located at 650 and 830 nm exhibits different profiles as shown in the inset in Figure 1. Consequently, these absorptions assigned to the absorption of different species. The absorption component at 650 nm generated with decreasing of the monomeric absorption at 702 nm around 30 vol % of MeOH, while growing of the absorption at 830 nm occurred with decreasing of the absorbance at 650 nm about the MeOH contents over 60 vol %. Further increasing of the proportion of the poor solvent results in the development of the two bands. These facts indicate that the absorption component at 650 nm is a superposition of the absorption bands of a cofacially-stacked aggregates[10] having an absorption maximum around 650 nm and slipped-stacked forms with the two peaks at 650 and 830 nm. Similar observation was obtained from the same experiments using compound **2**. Thus, we measured X-ray diffraction (XRD) of **1** to estimate structural feature of the slipped-stacked forms. The XRD pattern was characterized by four sharp diffraction lines at *d* spacing of 2.05, 1.79, 1.26, and 1.04 nm. The *hkl* indexation of these lines are characteristic of a 2-D rectangular packing of the column with lattice constants *a* = 3.95 and *b* = 2.05 nm.[11] Judging from these results, the cofacially-stacked aggregates of **1** further organized into a columnar aggregates even at its nonplanar structure. The mean stacking period in disk-like molecules without any groups normal to the molecular plane is usually 0.34 to 0.36 nm,[2] but because of the presence of the axial oxygen, compound **1** did not show clear evidence for the periodicity between the aromatic cores. According to the studies considering the
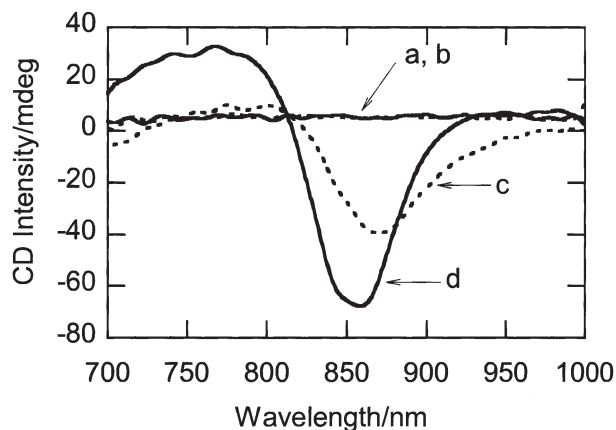
Figure 2. CD spectra of **1** ([**1**] = 8.1×10^{-6} mol dm^{-3}) in the mixture of CHCl$_3$ and MeOH with vol % of MeOH at (a) 0, (b) 60, (c) 70, and (d) 75 vol %.

spectral feature of the phthalocyanine aggregates, the Q-bands of **1** in a poor solvent is ascribed to the slipped-stacked forms.[12] This assumption is in agreement with the XRD result that indicates staggered assembly of the phthalocyanine cores in a column. When a chiral superstructure is present, this should result in a circular dichroism (CD) activity. Therefore, we examined CD measurements of **1** as a spin-coated film and in CHCl$_3$. As reported for several chiral phthalocyanines, the films of **1** showing intense CD signal at the entire absorption region, while a CHCl$_3$ solution of **1** gave weak CD signals even at high concentrations.[2] This suggests the CD activity in the films must result from the chiral aggregation of **1** molecules. Hence, to clarify the chiral aggregation nature, we measured CD spectrum of **1** in the mixture of CHCl$_3$ and MeOH. Figure 2 shows the CD spectra of **1** in the mixture from the visible to NIR region. As described for the CD of a CHCl$_3$ solution of **1**, the mixtures exhibiting larger proportion of the monomeric absorption were practically CD inactive. While the solution containing larger vol % of MeOH (70 and 75 vol %) showed a change of CD sign around 800–850 nm. In reference to the absorption spectrum in Figure 1, the sign of CD spectrum in the Q-absorption region roughly changed from negative to positive on going from longer to shorter wavelength. These bands correspond to the split of the Q-bands of aggregates, suggests that the phthalocyanines stack into a left-handed helix in an aggregate.[2,13] The results obtained here indicate that **1** molecules spontaneously stack into the cofacially-stacked aggregates, and the aggregates assembled into slipped-stacked forms upon increasing of a proportion of the poor solvents. Furthermore, the XRD measurement of the film suggests the chiral columns expected to align into 2-D rectangular phase. Unfortunately, helical periodicity along the columnar stacks was not detected from the XRD of the films. In our third-harmonic generation (THG) experiments,[14] a spin-coated film of **1** with a thickness ca. 50 nm exhibited intense third-harmonic and the $\chi^{(3)}$ value of the film is 6.7×10^{-11} esu at a fundamental wavelength of 1907 nm with reference to fused silica substrates $(1.4 \times 10^{-14}$ esu).[6] A spin-coated film of compound **2** gave the $\chi^{(3)}$ value of 3.8×10^{-11} esu under the same conditions. Owing to an agreement of the $\chi^{(3)}$ phase factor, ϕ, of **1** and **2** films at $\phi = 90°$, these $\chi^{(3)}$ values are directly comparable. This suggest the enhanced $\chi^{(3)}$ value in **1** film must result not the simple res-

onance enhancement[15] but from the chiral assembly. One possible reason that shows the enhancement of third-order nonlinearity is side-chain uniformity in **1** relative to **2**.

In summary, a chiral phtahlocyanine derivative **1** is shown to form columnar packing with a left-handed helical assembly. Because of the decreasing of cofacial interactions between aromatic cores, **1** exhibits the phase II-like absorptions at the NIR region with CD activity. It is noteworthy that chiral phthalocyanine **1** gave better third-order NLO responses relative to the achiral analogue, compound **2**, through the chiral aggregation. From this, a chiral molecule **1** is a potential candidate for the chiral NLO materials.

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8   Data for **1**: Elemental analysis calcd (%) for C$_{72}$H$_{96}$N$_8$O$_9$V: C 68.17, H 7.63, N 8.83, O 11.35, V 4.02; found, C 68.47, H 7.63, N 8.60; FAB–MS (3-NBA) calcd, 1267.80, found, 1267.183; UV–vis (CHCl$_3$) λ_{max}, nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 702 (5.31), 632 (4.52), 438 (4.59), 345 (4.84); $[\alpha]_D = -1632.9°$ ($c = 0.01$, CHCl$_3$, 25 °C).
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