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Crystal Structures of Dyes Composed of an Aniline Donor and a Pyrroline-Type Acceptor

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Abstract

Single crystals of 3-[4-(dibutylamino)phenyl]-4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline **1a** and its derivatives with 1-butyl (**1b**), 1-hexyl (**1c**) and 1-(2-[2-(acryloyloxy)ethoxy]ethyl) (**1e**) groups were prepared and their X-ray crystallographic analyses were performed. These dyes have a common π -conjugation system terminated by donor and acceptor groups, and they can be applied to use as electrooptic chromophores. Their absorption of the crystals were discussed in relation to the chromophore alignment in the crystals. Antiparallel interaction between the π -conjugated systems, whether face-to-face or side-by-side, caused absorption shifts to shorter wavelengths. Absorption at the longest wavelength was observed for **1e**, whose π -conjugated systems were separated by the substituents resulting in almost no interaction among the adjacent π -conjugated systems.

Key-words: Dye, Crystal structure

1. Introduction

For large-capacity information processing, ultrafast switching devices are required, and one of the promising candidates is electrooptic (EO) devices, in which optical signals are switched by applying electric field. Especially, organic compounds generally with low dielectric constants are suitable for the EO materials. In addition, polymers are advantageous in processability to fabricate optical waveguides including EO devices. Thus, development of practical EO polymers has been continued since 1980s¹⁻³⁾. EO polymers are usually composed of matrix polymers and EO chromophores, which are dispersed in the polymers or covalently bonded to the polymers. EO chromophores should have large first hyperpolarizabilities (β s). Also they should have large dipole moments (μ s) because the EO effect only appears in noncentrosymmetric structures and EO chromophores in polymer matrices must be aligned in polar orientation by applying DC electric field, i.e., poling. However, large μ causes dipole-dipole interaction to form antiparallel dimers and aggregates resulting in canceling out of dipole moments.

Recently, chromophores with a donor group and 4-cyano-5-dicyanomethylene-2-oxo-3-pyrroline-3-yl (CDCOP) group as an acceptor have attracted attention as EO dyes⁴⁻⁷⁾. Such CDCOP derivatives have been reported over 50 years ago^{8,9)}.

The CDCOP group is a strong acceptor since three cyano and one oxo groups are conjugated in the group. Furthermore, the CDCOP group composed of a five-membered ring reduces steric hindrance to the linked aromatic ring, resulting in a planar structure responsible for the fully conjugated structure. Meanwhile, when the CDCOP dyes were dispersed in polymer matrices, their UV-vis absorption spectra were often different from those obtained in solution suggesting that the dyes were aggregated in the polymers. Such aggregation avoids efficient poling, and investigation on the aggregation states of the dyes is important. In this study, we grew single crystals of some CDCOP dyes with different substituents and their crystallographic analyses were conducted. Since molecular alignment in a crystal must be a typical example for aggregation states of the molecule, crystal structure analyses of the dyes may be helpful to consider the aggregation in the polymers. We also discussed the relationship between the crystal structures and the corresponding UV-visible diffuse reflectance spectra.

2. Experimental

2.1 Synthesis of compounds

CDCOP derivatives were synthesized according to the scheme in Fig. 1. The detailed procedures are described below.

1a: The mixture of **2**¹⁰⁾ (4.0 g, 17.2 mmol) and *N,N*-dibutylaniline **3** (4.4 g, 20.0 mmol) in DMF (40 mL) was stirred with cooling by an ice bath. To this, phosphoryl chloride (4.8 mL, 52 mmol) was added dropwise, and stirring

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