A High-contrast Dichroic Crystal: A New Metal-containing Tecton with Hybrid Coordination- and Hydrogen-bonding Interactions

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A newly discovered crystalline material showed high-contrast dichroism. The arrangement of the chromophore in the crystal fairly accounts for the angular dependence of the light absorption. This material demonstrates a new application of metal-containing supramolecular architectures to wave optics.

Optically anisotropic materials, such as dichroic dyes, show dichroism for polarized light and hence play an important role in wave optics. To exhibit dichroism, a dye must have specific axial anisotropy of molecular orientation in the crystalline or mesophase structure. Recently, attempts to fabricate dichroic materials have become increasingly sophisticated: for example, researchers have used the dispersion of nanoparticles or organic semiconductors into polymer films,[1,2] guest–host interactions in anisotropic media like liquid crystals or clay,[3–5] and self-assembly induced by van der Waals and solvophobic interactions.[6–8]

For more than 50 years, it has been known that some crystalline metal complexes show dichroism.[9] While crystalline materials are thermally stable and easy to handle, the engineering of organic crystals is often difficult because dipole–dipole interactions can contribute to the elimination of macroscopic anisotropy. A strategy involving the combination of coordination-bonding and hydrogen-bonding interactions, has been used to provide multiple recognition sites in supramolecular chemistry,[10] and this strategy is also being applied to crystal engineering.[11] However, orthogonality between these interactions is indispensable for the construction of well-defined and predictable structures.[12]

In this study, we investigated a strategy involving the in situ formation of a metal-containing tecton to construct a novel organic–inorganic hybrid crystal that shows high-contrast dichroism for visible light. This crystal was composed of a nickel(II) complex (NiL_2) of a 1-naphthylmethylidene Schiff base (Figure 1). This complex served as a supramolecular tecton with self-complementary hydrogen-bonding sites, and it formed a ladder-like hydrogen-bonded strand. Analysis of the crystal structure revealed that the strands aligned in one direction and that the overall arrangement of the chromophore was responsible for the optical anisotropy.

A Schiff base ligand (HL) was synthesized from 2,6-dihydroxynaphthalen-1-carbaldehyde and *n*-octylamine (69%) and then mixed with nickel(II) salt to afford greenish brown prismatic crystals (47%).[13] X-ray crystal structure analysis of the crystals revealed that hydrogen bonds between the OH group of the ligand and the O(–Ni) atom (the O···O bond length was 2.791 Å) formed a ladder running along the *b* axis (Figure 2a). At 298 K, the unit complex was a centrosymmetric NiL_2 molecule with disordered alkyl chains, whereas at 193 K the two alkyl chains adopted different conformations in a unit cell with a volume twice that at 298 K. Some hydrogen atoms in alkyl chains have close contacts with naphthalene rings: implying intra- and intermolecular CH/π interactions (Figure S1).[13] These crystal structures suggest that the spatial extension of the alkyl chains was suitable for unidirectional alignment of the ladders, and there was a space for the alkyl chains to fluctuate to some extent between the running ladders.

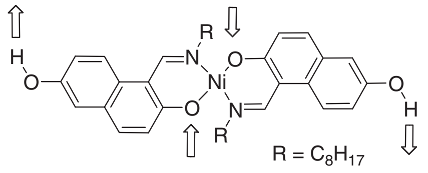

Figure 1. Structure of NiL_2. The arrows indicate the direction of hydrogen bond donation.

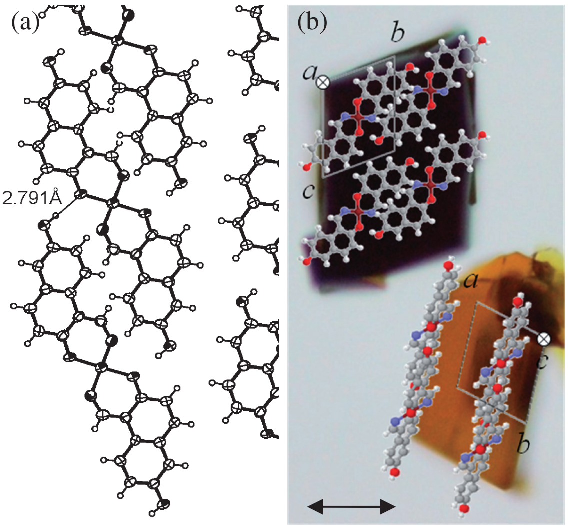

Figure 2. (a) Hydrogen-bonded ladder of NiL_2 in the crystalline state. Alkyl chains are omitted for clarity. (b) Optical micrographs of NiL_2 crystals, with superimposed crystal structures. The double arrow indicates the polarization of the incident light.

Under irradiation with polarized light, the color of the crystal observed by optical microscopy depended on the orientation of the crystal relative to the optical axis (Figure 2b). Because the apparent dihedral angles of the crystal facets agreed fairly well with the angles ($\alpha = 107.16$, $\beta = 103.54$, $\gamma = 98.51°$) of the unit cell determined from the crystal structure at 298 K, we assigned the cell orientation shown in Figure 2b. The superimposition shown in Figure 2b indicates that the molecular plane of the Ni complex was nearly parallel to the *A* plane and nearly perpendicular to the *B* and *C* planes. The crystalline facets vertical to the *a* axis appeared dark brown. In contrast, the facets vertical to the *c* axis appeared yellowish orange when the polarization of the light was perpendicular to the *b* axis.

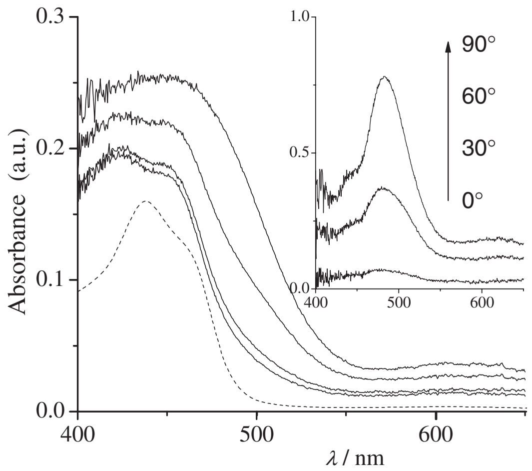

Figure 3. Absorption spectra of NiL_2 in the solid state (crystal, solid line) and in chloroform (2×10^{-5} M, dashed line). Inset: Solid-state spectra for various polarization angles with the spectra for 0° subtracted.

For a crystal with appropriate size, solid-state UV–visible (UV–vis) spectra were recorded through an optical microscope equipped with an optical fiber connected to a UV–vis spectrometer. The crystal was aligned so that its *c* axis coincided with the optical axis, and the polarizer was rotated from 0 to 360° in 30° steps. The baseline was corrected for every rotation angle to eliminate the effect of partial polarization of the light source. At 400–650 nm, the spectral profile was similar to that measured in chloroform (Figure 3). A band at 400–500 nm was attributed to overlapping of the π–π^* and charge-transfer transitions between the metal and the ligand, whereas a broad absorption at around 600 nm was attributed to a d–d transition. The spectral profile varied with the rotation angle of the polarizer, particularly at around 481 and 610 nm (Figure 3, inset).

The values of absorbance at 500 nm are plotted against the rotation angle in a polar coordinate system in Figure 4 (see Figure S2 for plots in a Cartesian coordinate system),[13] in which the alignment of the cell system relative to the polarizer is indicated. The plot exhibited a clearly dipolar shape with its maxima pointing perpendicular to the *a* axis, that is, roughly parallel to the N_2O_2 square plane of the Ni complex. At this angle, the facet appeared dark brown, similar to the facet of the *A* plane. Consequently, the dark brown color of the crystal was related to transition(s) whose transition moment vector is laid in the coordination plane. If we assume D_{2h} symmetry for the local $Ni(N_2O_2)$ moiety, this condition fits $^1A_g \rightarrow {}^1B_{2u}$ or $^1A_g \rightarrow {}^1B_{3u}$ transitions, which we interpreted as metal-to-ligand charge-transfer transitions from a d_{xy} orbital of Ni to σ^* orbitals of Ni–O and Ni–N bonds, or as ligand-to-metal charge-transfer transitions from σ orbitals of Ni–O and Ni–N bonds to a $d_{x^2-y^2}$ orbital. More details regarding the assignment are under investigation.

These preliminary results demonstrate a new application of metal-containing supramolecular architectures to wave optics; this application makes full use of a molecular design involving hybrid coordination bonding and hydrogen bonding and takes advantages of the superior optical properties of a metal complex. Other combinations of metal ions and amine side chains can be expected to increase the variety of such materials.

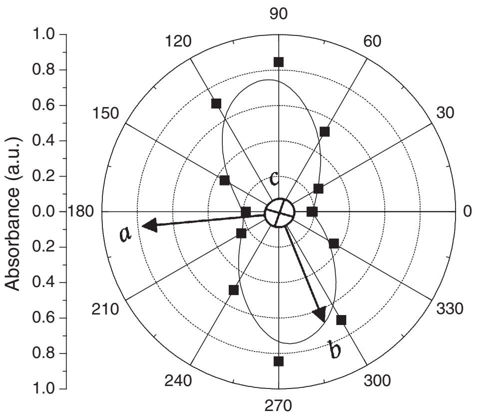

Figure 4. Plot of absorbance at 500 nm against rotation angle.

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13 The synthetic details and characterization data of HL and NiL_2 are available as Supporting Information on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html. Regarding crystallographic information format (CIF) files for NiL_2 (at 298 K and at 193 K), are deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-723444, 723445. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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