Tetra(*tert*-butyl)phthalocyanine Copper–Iodine Complex Film with Large Dichroism induced by Shear

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A unidirectional arrangement of phthalocyanine molecules at a 'material level' is achieved by shearing phthalocyanine–iodine complex, giving a new dichroic phthalocyanine film.

Phthalocyanine is a planar molecule with one metal atom at its centre and many π electrons on its molecular plane. Its novel structure is the cause of its semiconductivity,[1] photoconductivity[2] and dichroism.[3] However, phthalocyanine at a 'material level' exhibits no electrical properties and no optical anisotropy, because the molecules do not stack with the same orientation [Fig. 1(*a*)]. Much attention has been focused recently on the design of unidirectional arrangements or cofacial stacking structures [Fig. 1(*b*)] by techniques including Langmuir–Blodgett,[4] chemical modification by introduction of a liquid crystal[5] and growth of a single crystal.[6] Here we report on a unidirectional arrangement of phthalocyanine molecules by shear force.

The phthalocyanine material in this work was tetra(*tert*-butyl)phthalocyanine copper–iodine (PhtalCu–I) complex, prepared by mixing solutions of tetra(*tert*-butyl)phthalocyanine copper (100 mg) and iodine (40 mg) in dichloroethane (1 ml). The composition of the complex obtained (dried Ar stream, 24 h) was $(\mathrm{PhtalCu})_1(\mathrm{I})_{1.37}$ by elemental analysis (Found: C, 59.17; H, 4.95; N, 10.67%). According to our laser Raman spectroscopic measurements,† linear polyiodines[7,8] of I_3^- (114.0 cm^{-1}) and I_5^- (168.0 cm^{-1}) existed in the complex. EPR studies indicated no oxidation of Cu^{2+} of phthalocyanine molecules in the complex and there was no difference in intensity between EPR spectra of tetra(*tert*-butyl)phthalocyanine copper before and after the formation of the complex, suggesting that the PhtalCu–I complex was formed by a charge transfer of iodine and ligand of phthalocyanine. The EPR spectrum of the complex had a single line‡ and no hyperfine structure, indicating that the phthalocyanine molecules condensed in the complex.[9] From DSC data no thermal transition was detected below 380 °C, at which temperature the complex decomposed exothermally.

The PhtalCu–I film was prepared by the following procedure. The PhtalCu–I complex was sandwiched between two glass plates. Shear force was then applied to the complex by sliding the glass plates over each other. The sheared complex was finally dried *in vacuo* at room temperature, giving a blue PhtalCu–I film *ca.* 50 μm thick.

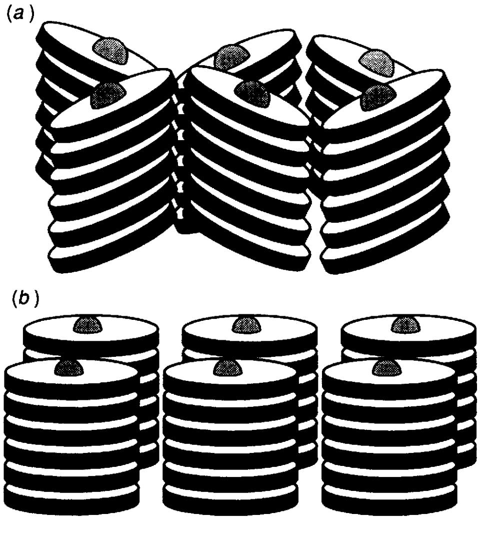

Fig. 1 (*a*) Diagonal stacking of phthalocyanine molecules and (*b*) cofacial stacking structure

In Fig. 2, *x* and *y* indicate vibration directions of the incident light on the PhthalCu–I film corresponding to directions parallel and perpendicular to the applied shear force, respectively. The film appears to be colourless in the *x* direction, but blue in the *y* direction.

Fig. 3(*a*) shows the polarized visible transmission spectra of the PhtalCu–I film prepared under shear. The light with vibration in the *x* direction passes through the film in the wavelength range from 450 to 700 nm (broken line). In the *y* direction light is fully absorbed between 525 and 675 nm, but blue light (450–500 nm) is transmitted by 20% (solid line). The analogous spectra prepared without shear are shown in Fig. 3(*b*). Light with vibration in both of the *x* and *y* directions passes through the film. It can be concluded, therefore, that the dichroism is induced by shear force. The absorption peaks of the π–π^* transition of phthalocyanine due to the transition moment parallel to its molecular plane appear at wavelengths from 600 to 700 nm.[10] As shown in Fig. 3(*a*), the polarized light with vibration in the *y* direction is absorbed by the film between 550 and 700 nm, but in direction *x* the same wavelength range passes through the film. It is suggested that phthalocyanine molecules in the film set their molecular planes perpendicular to the shear force by an action of shear force.

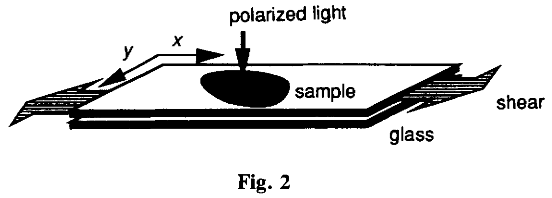

Fig. 2

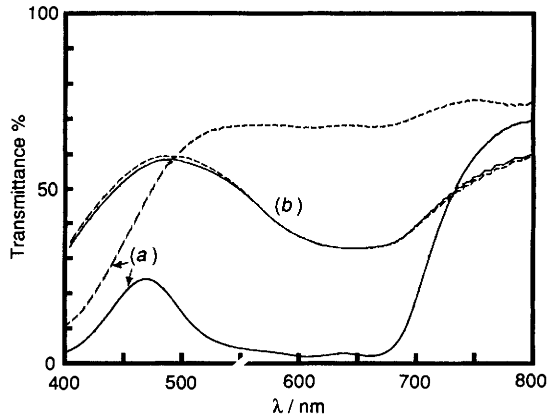

Fig. 3 Polarized visible transmission spectra of the films prepared (*a*) under the influence of shear and (*b*) without shear. The broken and solid lines represent spectra of the polarized light with vibration in the *x* and *y* directions, respectively.

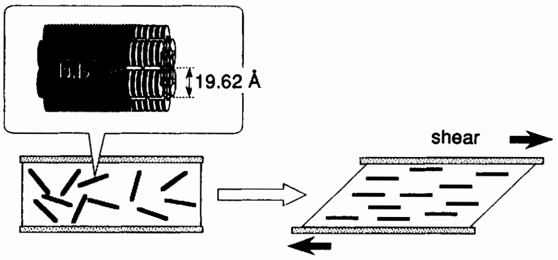

Fig. 4 Schematic illustration of a mechanism for the shear induced unidirectional arrangement of molecules in the PhtalCu–I film

The dichroic ratios, defined by the intensity ratio of x to y, are 10.1 at 610 nm and 9.4 at 670 nm. These values are nearly equal to those of the traditional polarizers of poly(vinyl alcohol)–iodine complex films.[11]

Next we made laser Raman spectroscopic or X-ray diffraction measurements§ on the film to investigate the configuration of molecules in the PhtalCu–I film. Laser beam irradiation in direction x gave two raman peaks at 114 and 168 cm^{-1}, but none in the direction y, indicating that linear polyiodines of I_3^- and I_5^- run parallel to the direction of the shear force. Diffractions from (100), (110) and (210) planes¶ were detected in both the x and y directions, which may be derived from Cu atom in phthalocyanine. The X-ray diffraction data indicate that the lattice structure of phthalocyanine is a hexagonal system with an unit cell length of 19.62 Å.

From the experimental results, we here propose the shear induced dichroism (Fig. 4): the EPR spectrum suggests that phthalocyanine molecules condense in the complex as bundles of columns. The X-ray diffraction studies indicate that the columns form a hexagonal lattice. We maintain that the phthalocyanine molecules are already stacked in columns, with polyiodines existing among them, dispersed at random, then oriented unidirectionally by the action of a shear force. This arrangement is supported by our laser raman studies. The new technique has allowed us to design a dichroic phthalocyanine film.

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Footnotes

† The experiments were carried out using a laser Raman spectrometer (JASCO NR-1000S, Ar$^+$ excitation ν_0 = 5145 Å).

‡ Tetra(*tert*-butyl)phthalocyanine copper (ΔH = 360G, g = 2.062), PhtalCu–I complex ($\Delta H_{\parallel}$ = 400G, $g_{\parallel}$ = 2.090; $\Delta H_{\perp}$ = 200G, $g_{\perp}$ = 2.040).

§ A Rigaku diffractometer RAD 2B(Cu/Kα) was used.

¶ d-Spacings of 16.7, 9.7 and 6.4 Å, respectively.

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