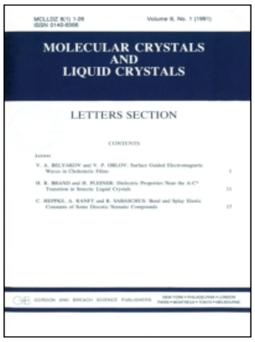

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Optical and electrical characteristics of solvent-extracted and anisole-insoluble dyes obtained from coal tar pitch

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ABSTRACT
We investigated the photoluminescence-excitation spectrum and the hole mobility of solvent-extracted CTP (coal tar pitch). The hole mobility increased with more ordered CTP as judged by the I_D/I_G ratio. In addition, anisole-insoluble CTPs with different softening points were also characterized. The chloroform- or DMSO-extract from the anisole-insoluble CTP with the higher softening point showed the more molecular order and the higher hole mobility than those of the CTP with the lower softening point. By using the CTP with the higher softening point, the highest hole mobility of 9.9×10^{-5} cm^2/Vs was observed when the dye extracted with DMSO from the anisole-insoluble CTP was used.

KEYWORDS
Coal tar pitch; Raman spectrum; SCLC mobility; Photoluminescence peak wavelength; Solvent extraction; Insoluble dye

Introduction

A coal, one of the most important energy source, contains a coal tar pitch (CTP) as a byproduct in the production of the coke, in 5–10% of the coal weight. The large amount of the CTP has been produced all over the world, and was used as the raw material for the production of pitch-based carbon fibers [1, 2]. Thus, an effective and practical use of the CTP has been an important problem to be solved. Nowadays, there have been several investigations, such as carbon electrodes for Li-ion batteries [3] and supercapacitors [4] as novel applications of the CTPs.

Recently, our group demonstrated an optical application of the CTP as an emissive layer of an organic light-emitting diode (OLED) with the solvent-extracted dye from the CTP [5]. Since the CTP contains many types of low molecular-weight π-conjugated compounds, the extracted dyes exhibit the visible emission by irradiating the ultraviolet (UV) light or injecting the carrier from a sandwiched electrodes. By now, the photoluminescence (PL) characteristics have been found to be controlled by the selective extraction with various solvents or the chromatographic separation [6]. In addition, several extraction techniques have been investigated to obtain suitable dyes from CTPs [6, 7]. To understand the physical characteristics of extracted CTPs, several measurement techniques, such as Raman [8, 9] and Fourier transform infrared [10, 11] spectroscopies, have been investigated. However, the detailed properties of

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extracted dyes have been unknown to discuss optical and electrical characteristics in the CTP layer.

In this study, we investigated the PL-excitation spectrum of the solvent-extracted CTP and the hole mobility estimated from the space charge limited current method as optical and electrical characteristics, respectively. In addition, the structural order of the CTP thin film was estimated from the Raman spectrum. These data showed an influence of the molecular order on electrical property of CTP.

Experimental method

We used two kinds of CTPs, defined as P1 and P2, with different softening points, where the softening points of P1 and P2 CTPs were approximately 90 and 280°C, respectively. The softening point can be controlled by a conventional air-blown method [12–16]. The P2 powder was first dissolved into acetone, ethanol, cyclohexane, 1-propanol, chloroform, and anisole at a concentration of 10 mg/mL, and the resulting suspension was stirred for 72 h. Then, the obtained suspension was centrifuged to remove insoluble dyes. Finally, the obtained suspension was centrifuged at 6000 rpm for 10 min to remove insoluble dyes. The PL-excitation spectrum and the hole mobility of the supernatant solution were measured. Separately, the P1 and P2 CTPs were also extracted with anisole for 72 h, and the insoluble dye was obtained as a solid with the same centrifugation process. The anisole-insoluble dye was then stirred in DMSO or chloroform for 72 h. Then, the obtained suspension was centrifuged at the above-mentioned condition. The PL-excitation spectrum and the hole mobility of the resulting supernatant were measured.

The Raman spectra were acquired using an inVia Raman microscope (Renishaw) with the excitation at 532 nm wavelength. The PL-excitation spectra were recorded on a spectrofluorometer (FP-6200, JASCO). The electrical characteristics were measured as the hole mobility, which was calculated from the space charge limited current density (SCLC) method [17]. The device for the measurement of mobility consisted of indium tin oxide / poly(3,4-ethylenedioxythiophene:polystyrene sulfonate (40 nm) / CTP / MoO_3 (20 nm) / LiF (0.5 nm) /Al (100 nm) layers, where the CTP layer was spin-coated at 2000 rpm for 60 s.

Results and discussion

Figures 1 shows Raman spectra of the solvent-extracted P2-CTPs with acetone, ethanol, cyclohexane, 1-propanol, chloroform, and anisole as solvents. Two components in the Raman spectrum correspond to the G band at around 1580 cm^{-1} and the D band at around 1350 cm^{-1}. The experimental result in Figure 1 shows that two Raman bands were observed for all the samples. The G band attributes to the E_{2g} symmetry of carbon, and contains the in-plane bond-stretching motion of carbon sp^2 atoms [18, 19]. In addition, the D band is originated from the amorphous carbon. As a result, the intensity ratio of G and D bands implies the molecular order of the CTP layer. The I_D/I_G ratios were calculated as 0.76 (acetone), 0.76 (ethanol), 0.65 (cyclohexane), 0.65 (1-propanol), 0.60 (chloroform), and 0.59 (anisole). The lower value corresponds to the molecular order along the in-plain direction.

Table 1 shows the relationship between the peak wavelength of the PL spectrum and the I_D/I_G ratio. The PL peak wavelength was estimated from the PL-excitation spectrum, and was shifted toward the longer wavelength region with decreasing I_D/I_G ratio. This result indicates that the anisole- and chloroform-extracted CTPs showed the relatively longer PL peak wavelength, and this phenomena seems to relate to the molecular order of extracted CTP as

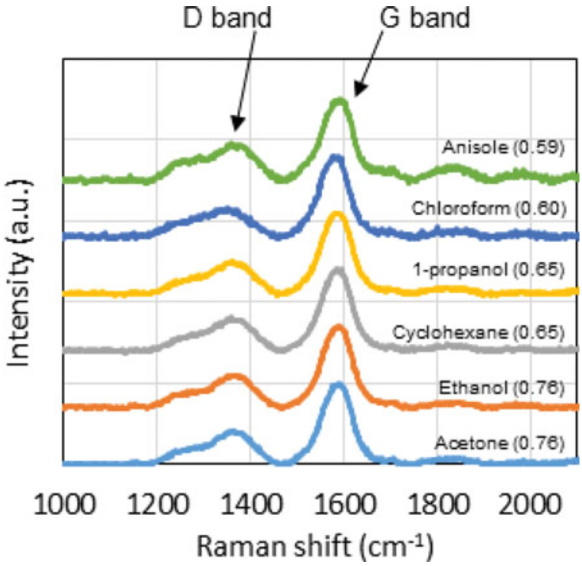

Figure 1. Raman spectra of solvent-extracted dyes from P2 CTPs (I_D/I_G ratio for each solvent are in parentheses).

observed the smaller I_D/I_G. In addition, the SCLC mobility also showed the clear relationship with the I_D/I_G ratio, as shown in Table 1. In general, the Raman signal at 1380 cm^{-1} (D band) of carbon-based materials indicates the disorder mode of carbon. That is, the high I_D/I_G ratio corresponds to the relatively random molecular orientation of the carbon material. Therefore, this result indicates that the amorphous carbon material prevents the efficient carrier transport, resulting in the lower SCLC mobility. On the other word, the I_D/I_G can be controlled by changing the extracted solvent, resulting in the change of the carrier mobility.

Figure 2 shows the PL-excitation spectra of anisole-insoluble dyes, which were defined as P1-C, P1-D, P2-C, and P2-D (P1: CTP with the lower-softening point, P2: CTP with the higher-softening point, C: extracted from the anisole-insoluble dye with chloroform, D: extracted from the anisole-insoluble dye with DMSO). By comparing the P1 and P2 CTPs, the shorter excitation band at below 400 nm disappeared for the P2 CTP. Since the higher softening point of P2 than that of the P1 indicated the P2 contained larger π-conjugated molecules, and the excitation band width of P2 became narrower during the air-blown process.

Table 2 summarizes the SCLC mobility and the I_D/I_G ratio of anisole-insoluble dyes P1-C, P1-D, P2-C, and P2-D (same to Table 1). In both cases of P1 and P2 CTPs, the higher SCLC hole mobilities of CTPs were obtained with DMSO solvent than those obtained with chloroform solvent (P1-C vs. P1-D, P2-C vs. P2-D). Similarly, in both cases of DMSO- and chloroform-extractions, the higher SCLC mobilities were obtained for the P2 CTPs (P1-C

Table 1. I_D/I_G ratio, PL peak wavelength, and SCLC mobility of solvent-extracted dyes from P2-CTP (I_D/I_G ratio was estimated from the Raman spectrum).

solvent	I_D/I_G	PL peak wavelength (nm)	SCLC mobility (10^{-5} cm^2/Vs)
anisole	0.59	554	4.67
chloroform	0.60	558	4.02
1-propanol	0.65	459	3.12
cyclohexane	0.65	472	3.22
ethanol	0.76	460	2.46
acetone	0.76	436	0.92

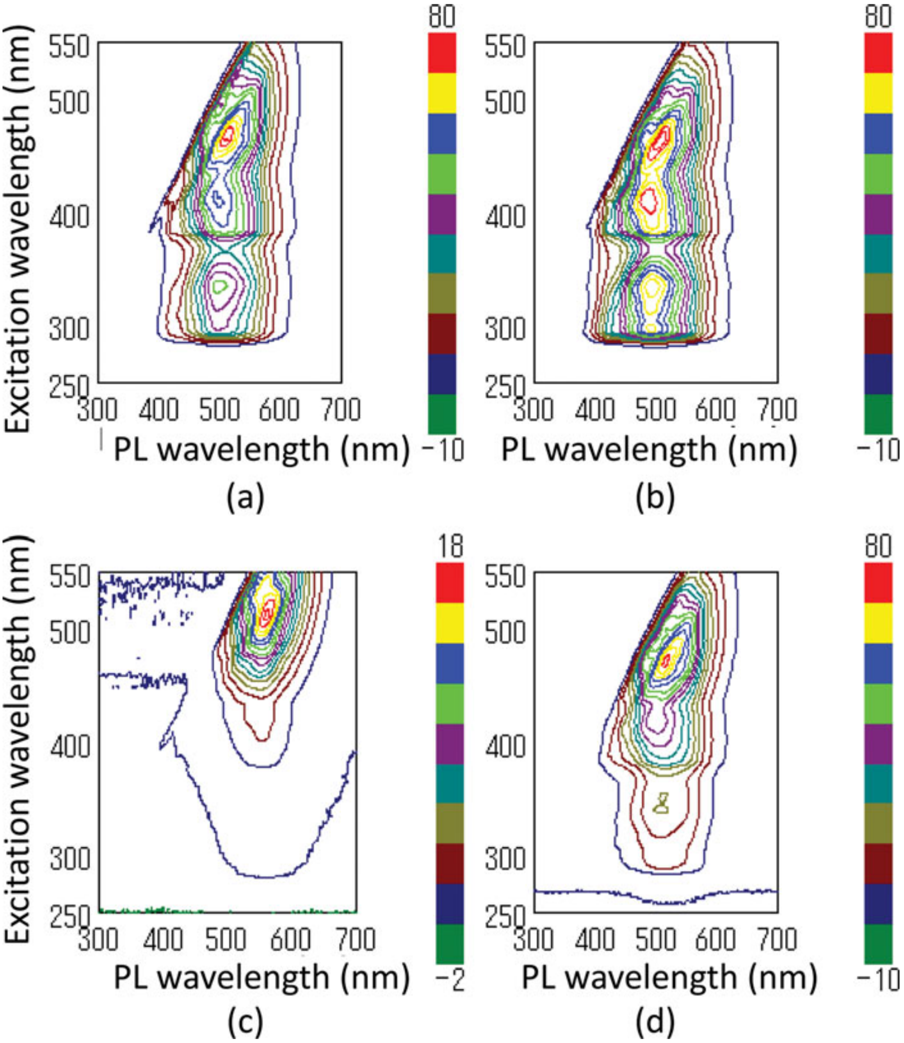

Figure 2. PL-excitation spectra of anisole-insoluble dyes from CTPs, (a) P1-C, (b) P1-D, (c) P2-C, and (d) P2-D.

vs. P2-C, P1-D vs. P2-D). As a result, the highest hole mobility of 9.9×10^{-5} cm^2/Vs was achieved for the P2-D CTP. Considering the relationship between the SCLC mobility and the I_D/I_G ratio, the higher SCLC mobility may come from lower the I_D/I_G ratio. That is, the lower I_D/I_G ratio, indicating the higher molecular order, causes the efficient carrier transport with the low scattering loss, resulting in the higher hole mobility. The high molecular order may also come from the stronger intermolecular interaction with larger π-conjugated molecules.

Table 2. SCLC mobility and I_D/I_G ratio estimated from the Raman spectrum of anisole-insoluble dyes from CTPs (P1-C, P1-D, P2-C, and P2-D).

	SCLC mobility (10^{-5} cm^2/Vs)	I_D/I_G
P1-C	2.4	0.77
P1-D	5.0	0.64
P2-C	7.8	0.63
P2-D	9.9	0.54

This result is good agreement with the tendency of the relationship between the PL peak wavelength and the I_D/I_G ratio in Table 1.

Conclusion

We investigated the molecular order of CTP thin film by the Raman spectroscopy, and the low I_D/I_G value was found to correspond to the long PL peak wavelength and the high SCLC mobility. Since the OLED application is one important application, this result is useful for controlling optical and electrical characteristics of CTPs.

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