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Novel Electrical and Optical Properties of Discotic Liquid Crystals,

Substituted Phthalocyanine Rare-Earth Metal Complexes

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Abstract

Alkylthio-group-substituted phthalocyanine rare-earth metal sandwich complexes such as bis[octakis(alkylthio)phthalocyanineato]europium(II) $\{[(C_nS)_8Pc]_2Eu\}$, bis[octakis(alkylthio)phthalocyaninato]lutetium(III) $\{[(C_nS)_8Pc]_2Lu\}$, bis[octakis(alkylthio)phthalocyaninato]terbium(III) $\{[(C_nS)_8Pc]_2Tb\}$ exhibit discotic liquid crystal phases.

Photoluminescence (PL) peaks of $[(C_nS)_8Pc]_2Eu$ were observed at around 400-600nm and 730nm in chloroform solution. However, the strong narrow emission of Eu^{3+} ion was not observed compared with other Eu-complexes. The intensity and the decay time of the PL peak depends strongly on the phase. They have been explained by taking electronic energy schemes of both phthalocyanine ligands and Eu^{3+} ion into consideration. The role of triplet exciton is also discussed.

In the photoconductivity (PC) spectra of $[(C_nS)_8Pc]_2Eu$ several peaks were observed corresponding to the absorption peaks. The behavior has been discussed in terms of carrier migration along the stack of phthalocyanine cores in the discotic phase.

Current-voltage characteristics and dielectric properties of these discotic liquid crystals have also been clarified.

Introduction

Recently discotic liquid crystals which are composed of disc-shaped molecules stacked in columnar structures have attracted much attention, because extremely large hole mobility was observed in the discotic phase [1-5]. Discotic liquid crystals have a potential technological importance due to their semiconducting properties combined with their processability. One-dimensional nature of the columnar structure along which the fast carrier transport takes place, also stimulated much interest from both scientific and practical view

points. It should also be mentioned that by designing the molecular structure of central core parts of discotic liquid crystal various functionalities are also expected.

In this paper, electrical and optical properties of discotic liquid crystals with metal phthalocyanine cores such as $\{[(C_nS)_8Pc]_2Eu\}$, $\{[(C_nS)_8Pc]_2Lu\}$, $\{[(C_nS)_8Pc]_2Tb\}$ are presented. The possibility of p- and n-type doping of Lutetium bis-phthalocyanine has been demonstrated by M. Maitrot et al. [6]. Here we show for the first time the C_{60} doping effect in thin film of C_{60} -doped $[(C_nS)_8Pc]_2Eu$.

Experimental

Molecular structures of alkylthio-group-substituted phthalocyanine rare-earth metal sandwich complexes such as bis[octakis(alkylthio)phthalocyanineato]europium(III), bis[octakis(alkylthio)phthalocyaninato]lutetium(III), bis[octakis(alkylthio)phthalocyaninato]terbium(III) are shown in Fig.1. Synthetic route is also shown in this figure.

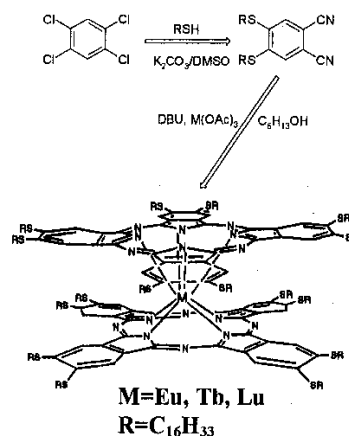


Fig.1 Synthetic route and chemical structure of $[(C_nS)_8Pc]_2M$.

Europium(III) acetate tetrahydrate in 1-hexanol was refluxed in the presence of DBU with stirring for 28 hours. A mixture of 5-bisdodecythiophthalonitrile was prepared by mixing 1-dodecylthiol and 4,5-dichlorophthalonitrile in dry DMSO. Europium (III) acetate tetrahydrate and DBU were added to the mixture. Then the mixture was refluxed for additional 16 hours and the reaction mixture was cooled down. The precipitate was separated by filtration and washed with methanol. The residue was purified by column chromatography and recrystallization twice from ethyl acetate. Detailed preparation and purification procedures and results of analysis were reported separately [7].

Liquid crystal phase of these compounds were optically observed utilizing an optical polarizing microscope equipped with a Mettler FP 82HT hot stage controlled by Mettler FP 90 Central Processor, with which phase transition temperatures

were also evaluated. X-ray diffraction spectra were also studied in solid and discotic liquid crystal phases with Rigaku RINT X-ray diffractometer.

Absorption and PL spectra measurements were carried out utilizing a Hewlett-Packard 8452A diode array spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer. Time resolved PL was studied utilizing femtosecond laser system. Femtosecond laser pulses were obtained from Ti:Sapphire mode-locked laser (Tsunami, Spectra-Physics) with pulse width of 80 fs and pulse trains of 82 MHz. The frequency is then doubled by a second harmonic generator unit utilizing barium beta borate crystals to obtain laser pulse with wavelength of 390 nm. The time-resolved PL spectra and PL decays were observed using a streak scope camera with temporal resolution of about 15 ps.

Photoconductivity was measured by the conventional method as already reported by the authors [8].

Dielectric constants and its temperature dependence of the sample in a sandwich cell were studied utilizing impedance analyzer (Yokogawa Hewlett Packard 4192A) and temperature controller (Shimaden, FP21).

Results and discussion

Figure 2 indicates phase transition temperatures of $[(C_nS)_8Pc]_2Ln$ as a function of the alkylthio chain length (n). As evident in this figure, this compound exhibits a discotic liquid crystal phase, Dh phase, in a relatively wide temperature range.

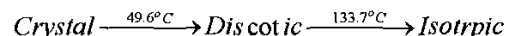


Fig.3 shows the large dielectric permittivities $\epsilon_{||}$ and ϵ_{\perp} in $[(C_nS)_8Pc]_2Eu$ in the liquid crystalline state measured at various frequencies.

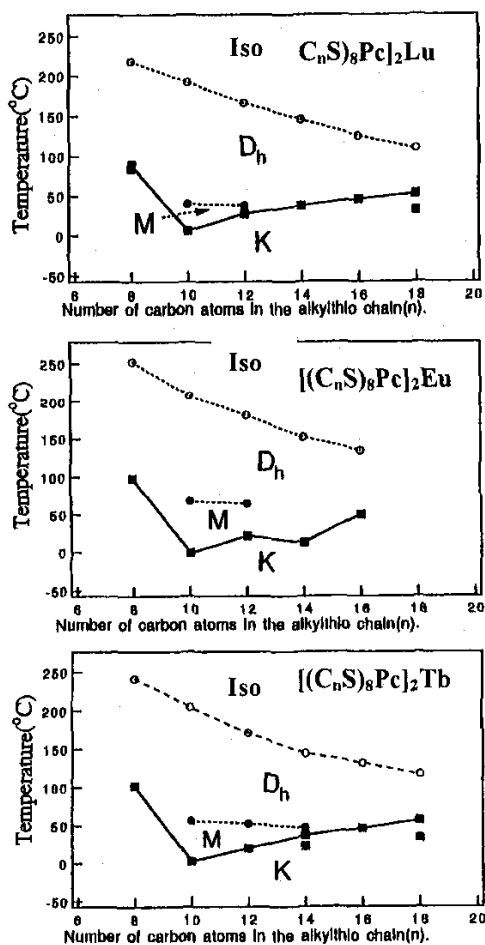


Fig.2 Phase transition temperatures of $[(C_nS)_8Pc]_2Ln$ as function of the alkylthio chain length (n).

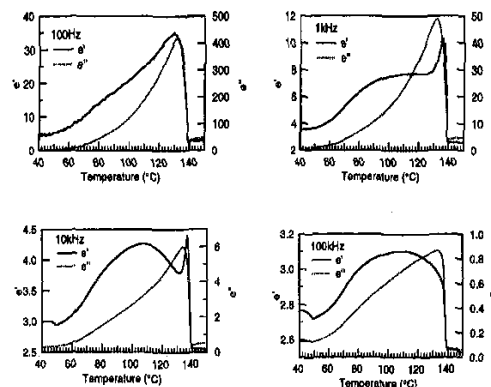


Fig.3 Dielectric permittivities $\epsilon_{||}$ and ϵ_{\perp} in $[(C_nS)_8Pc]_2Eu$ measured at various frequencies.

Figure 4 shows the optical absorption spectra of $[(C_nS)_8Pc]_2Eu$ in chloroform solution and a film. In this figure, two sets of absorption bands at 200~400 nm and 600~750 nm are clearly observed which is related to the Soret and Q-band of phthalocyanine. The several absorption peaks of Eu ion in visible range is too weak to be observed in absorption spectrum [9].

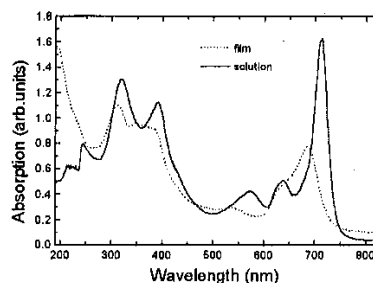


Fig.4 Absorption spectrum of $[(C_nS)_8Pc]_2Eu$ in solution in chloroform and thin film.

Figure 5 shows PL emission and excitation spectra of $[(C_nS)_8Pc]_2Eu$ in chloroform solution. PL was weak in comparison of metal free phthalocyanine in solution. However, it should be noted in this figure PL was observed both at around 400~600nm and at around 730nm, which may be related to the Soret and Q-bands of the absorption, respectively. The fine vibronic structure of higher energy emission band was observed in solution at room temperature. Generally in Eu-complex

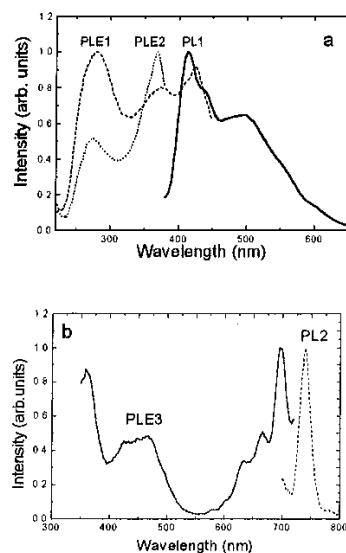


Fig. 5 (a) Photoluminescence emission (PL1) spectrum of $[(C_nS)_8Pc]_2Eu$ in chloroform solution in visible range and its excitation spectra for $\lambda_{em}=500nm$ (PLE1) and $\lambda_{em}=415nm$ (PLE2). (b) PL emission (PL2) in near IR region and its excitation spectra (PLE3, $\lambda_{em}=700 nm$).

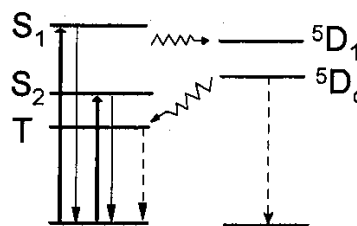


Fig. 6 Energy transfer processes in $[(C_nS)_8Pc]_2Eu$ (dashed lines represent less probable processes).

narrow line PL is observed at wavelength of about 615 nm.

The weak PL intensity suggests that in $[(C_nS)_8Pc]_2Eu$ the inter-system crossing from the singlet excited state to the triplet excited state should suppress the fluorescence strongly due to the large spin-orbit coupling in the presence of heavy Eu atom just as the case of Cu-phthalocyanine [10]. In Cu-phthalocyanine the fluorescence was totally suppressed and the phosphorescence was observed at around $1.12\mu m$. Indeed, the existence of the large spin-orbit coupling in bis(phthalocyaninato) lanthanide compounds has been shown experimentally [11]. This interpretation is reasonable if we take the energy levels of phthalocyanine π -electron system and f-electron states of Eu(III) into consideration (Fig.6). Direct excitation of Eu^{3+} ion has very low probability. Singlet energy transfer is also not significant [12]. Usually the narrow line emission of Eu^{3+} ion occurs by energy transfer through the triplet state of organic unit. However, in the case of $[(C_nS)_8Pc]_2Eu$ the lowest triplet state of $(C_nS)_8Pc$ is lower than the resonance levels of Eu^{3+} ion. Therefore, the triplet energy transfer to Eu^{3+} ion is impossible and the line emission of Eu^{3+} ion can not be observed. The experimental observation supports this mechanism. We should mention here that the photoluminescence of $[(C_nS)_8Pc]_2Lu$ is much higher than $[(C_nS)_8Pc]_2Eu$ since a 4f shell of Lu ion is filled [13]. A more detailed analysis of PL spectra will be published separately. The phosphorescence of $[(C_nS)_8Pc]_2Eu$ is under investigation.

Figure 7 shows the decay of PL in this compound observed by the time-resolved PL spectroscopy at room temperature. It should be mentioned that the photoexcitation occurs in the highest absorption band (Soret band). The broad weak photoluminescence band was observed in dilute solution. The PL was completely suppressed in the film. In solution the decay curve can be fitted by double exponent with $t_1=0.73 ns$ and $t_2=2.2 ns$.

Fig. 8 shows the strong photoluminescence quenching effect in chloroform solution of $[(C_nS)_8Pc]_2Eu$ at different concentrations. Normalized PL spectra were divided by concentration.

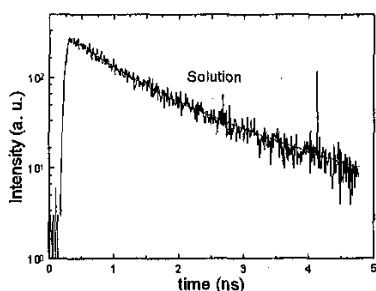


Fig. 7 The decay of photoluminescence of $[(C_{60}S)_8Pc]_2Eu$ in chloroform solution upon excitation with laser light of 390 nm at room temperature.

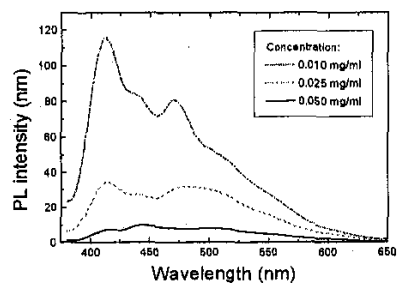


Fig. 8 Normalized photoluminescence spectra of $[(C_{60}S)_8Pc]_2Eu$ in chloroform solution at different concentrations.

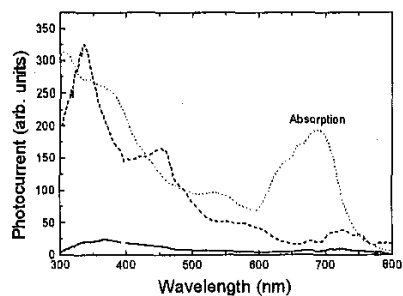


Fig. 9 Photocurrent spectra of undoped (solid line) and C_{60} -doped $[(C_{60}S)_8Pc]_2Eu$ (5 mol%, dashed line) and absorption spectra of undoped cast film (dotted line).

The C_{60} doping effect was also observed in thin film of C_{60} -doped $[(C_{60}S)_8Pc]_2Eu$. In Figure 9 we show the spectral dependence of photoconductivity of $[(C_{60}S)_8Pc]_2Eu$ before and after C_{60} doping and also absorption spectrum of undoped $[(C_{60}S)_8Pc]_2Eu$ obtained by casting from solution. The photoconductivity peaks at the Soret and Q-bands positions were observed in undoped $[(C_{60}S)_8Pc]_2Eu$. In the phthalocyanine compounds the photogeneration occurs through the dissociation of

a loosely bound exciton at some dissociation center or at the interface. The enhancement of photoconductivity in C_{60} -doped $[(C_{60}S)_8Pc]_2Eu$ is due to the efficient dissociation of excitons by C_{60} . The new strong peak at about 360 nm shows that the optical excitation at photon energy corresponding to the allowed transition ($h_{1u}-t_{1g}$) in C_{60} also induces remarkable photoconductivity. In this case, a hole will be transferred from C_{60} to $[(C_{60}S)_8Pc]_2Eu$. An excited electron on C_{60} relaxes into negative polaron on C_{60} .

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