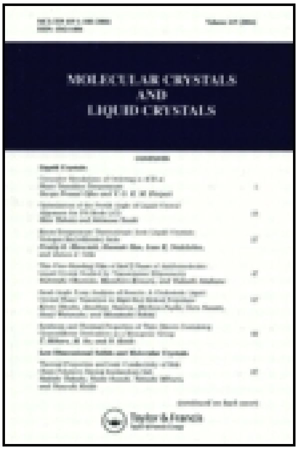

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Luminescence Study of Poly(3-Alkyl Ester Thiophene)s

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LUMINESCENCE STUDY OF POLY(3-ALKYL ESTER THIOPHENE)S

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Abstract Photoluminescence and quantum efficiency of poly(3-alkyl ester thiophene)s (PAETs) were investigated and compared with poly(3-octylthiophene) (POT). PAETs showed higher quantum efficiency than POT. Electroluminescent devices were fabricated using PAETs. A red-orange emission is observed above 12V forward bias.

INTRODUCTION

Conjugated polymers at their neutral states can be regarded as organic semiconductors[1] and the usages were well manifested in the light emitting diodes application.[2] The advantages over inorganic materials are easy fabrication processes and capability of color tuning by structural modification.[3]

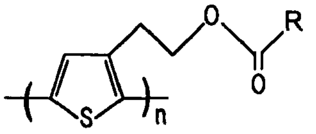
Polyalkylthiophenes (PATs) have been extensively studied due to their solubility and other interesting optical properties.[4] Modification of the structure is relatively easy and various substituents can be incorporated into PATs without losing the solubility.

In this paper, poly(alkyl ester thiophene)s (PAETs) were prepared and the effect of substituents on the luminescent properties were examined.

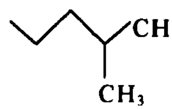
EXPERIMENTAL

PAETs were synthesized according to the reported method[5] and structures are shown below. Oxidative polymerization of the corresponding monomers produced about 60% head-to-tail coupled PAETs. Electronic absorption spectra were measured with Shimadzu 160A UV/Vis spectrophotometer. Luminescence spectra were recorded using a SPEX Fluoromax. And quantum yields of thin films were determined using

9,10-diphenylanthracene in poly(methyl methacrylate) (ϕ_{fl}=0.83) as standards.[6]



R = $-C_2H_5$ PPET R = $-C_9H_{19}$ PDET

R = $-C_4H_9$ PHET R =  PIVT

The light-emitting diodes consist of an indium/tin oxide (ITO) coated glass substrate, an emitting layer of PAET and aluminum electrode. For electroluminescence experiment, glass substrate with ITO electrode was cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol. Polymer in chloroform was coated on the ITO glass substrate using spin coater at a rate of 2000 rpm for 25 sec. Aluminum was deposited on the top of the polymer films as cathode at pressure below 2×10^{-5} torr. All the measurements mentioned above were performed at room temperature in air under DC bias conditions.

RESULTS AND DISCUSSION

From Figure 1, two absorption maxima were observed for PHET, PDET, and PIVT. The optical and electronic properties of PATs are generally associated with the conformational change and the conjugation length.[7] The overall red shift of absorption maxima and band edge can be interpreted as the existence of polythiophene segments with different conjugation length. Since the absorption and emission spectra of all PAETs in solution are almost identical, the difference of conjugation length are caused by the alkyl chain induced ordering of polythiophene in the solid state.

More drastic differences were observed in the emission spectra of PAETs (Figure 2). Excitation of PPET at 425nm gave emission peak at 636nm but from other PAETs emission maxima were observed at about 735nm. Considering that the intensity of absorption peaks at 436 and 484nm of PHET are about the same and excitation wavelength was at 425nm , an efficient energy transfer pathway should exist. The energy transfer from the excited state of polythiophene segment with a shorter conjugation length (higher energy state) to the excited state of the neighboring poly-

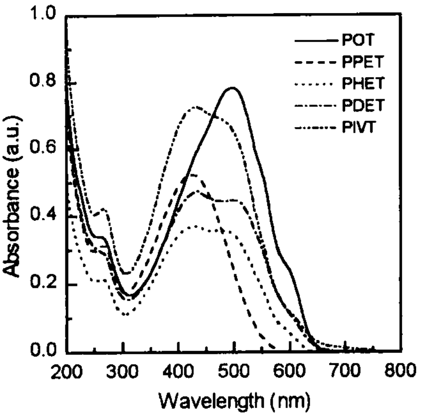


FIGURE 1 Absorption spectra of PAET films

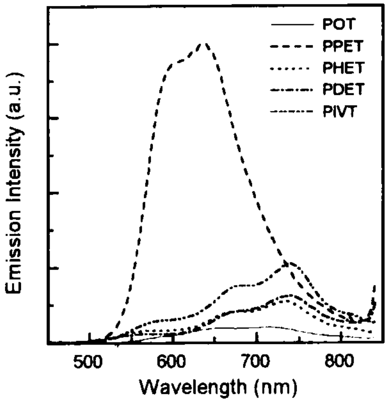


FIGURE 2 Emission spectra of PAET films

TABLE I Spectral properties of film of PATs excited at 425nm

	POT	PPET	PHET	PDET	PIVT
Absorption (λ_{max}, nm) (energy, eV)	500 (2.48)	427 (2.90)	436 , 484 (2.84)(2.56)	434 , 503 (2.86)(2.47)	436 (2.84)
Emission (λ_{max}, nm) (energy, eV)	712 (1.74)	602 , 636 (2.06)(1.95)	674 , 735 (1.84)(1.69)	674 , 738 (1.84)(1.68)	678 , 739 (1.83)(1.68)
Stokes' shift (eV)	0.74	0.84 , 0.95	1.00 , 0.87	1.02 , 0.79	1.01 , 1.16
Efficiency (ϕ_{fl})	0.0019	0.0268	0.0043	0.0045	0.0077

thiophene segment with a longer conjugation length (lower energy state) will readily occur. This process will also lower the luminescence efficiency.

Absorption and emission maxima along with fluorescence quantum efficiency and Stoke's shift of PAET films are listed in Table 1. PPET shows the highest quantum efficiency (ϕ_{fl}) among PAETs and PAETs have higher ϕ_{fl} than POT. According to Xu et al,[8] PATs with less coplanar structure in the ground state will have less chance to form excimers. Since the excimer tends to dissipate energy via the non-radiative pathway, more excimer formation will yield low ϕ_{fl}, which is consisted with the obervation.

Since ϕ_{fl} of PAETs is higher than that of POT, the carbonyl moiety in the ester group has no adverse effect on the fluorescence efficiency. Thus the carbonyl moiety in the side chain does not serve as a quenching site of the excited state.

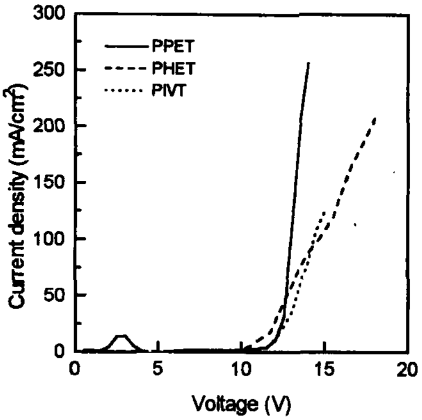


FIGURE 3 Current density vs voltage of characteristics of PAET diodes

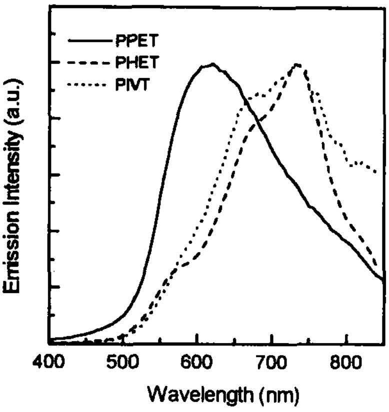


FIGURE 4 Electroluminescence spectra PAET diodes

The current-voltage(I-V) characteristics of PAET diodes are shown in Figure 3. The I-V curve shows typical diode characteristics and the threshold voltage is about 10-12 V. The forward bias current is obtained when the ITO electrode is positively biased and the aluminum electrode negatively. PPET has more steep slope than other PAETs, which indicates that the energy barrier of PPET is higher than that of other PAETs.[9]

The electroluminescence spectra of the PAET diodes are shown in Figure 4, which are very close to the corresponding photoluminescence spectra. PAET diodes emit light in orange-red region. Although electroluminescence efficiency of PAETs were not measured quantitatively, similar trends were observed in electroluminescence of PAETs and POT as in photoluminescence.

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