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Synthesis of light-emitting π-conjugated poly(pyrimido[5,4-*d*]-pyrimidine-2,6-diyl) with bulky side chains and high molecular weight

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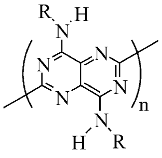
Abstract

New poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl) (PPympym) with bulky dialkylamino substituents (–NR_2, R = hexyl, decyl) was prepared by organometallic dehalogenative polycondensation using a zerovalent Ni complex. The obtained PPympym was soluble in common organic solvents such as $CHCl_3$ and THF, and GPC analysis (in $CHCl_3$; vs. polystyrene standards) indicated that new Ppympyms had high number-average molecular weights M_n of 19,100–34,000; they also gave a high $[\eta]$ value of about 2.1 dl g^{-1}. PPympym showed strong photoluminescence both in $CHCl_3$ and in film, and greenish-blue electroluminescence from PPympym-based double-layer light-emitting devices (ITO/PEDOTh/PPympym/Ca–Al; PEDOTh, poly(ethylenedioxythiophene)) was observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl); π-Conjugated polymer; Light-emitting properties

1. Introduction

π-Conjugated polymers are the subject of many recent papers [1–3]. Previously we reported preparation of new coplanar poly(naphthalene-2,6-diyl)-type π-conjugated polymer, poly(pyimido[5,4-*d*]pyrimidine-2,6-diyl), with nitrogen atoms at all of the *o*-positions by dehalogenative polycondensation using a zerovalent nickel complex [4,5]. The obtained polymers had number average molecular weights (M_ns) of 5000–10,000 with $[\eta]$ values of about 0.2 dl g^{-1}.



PPympym

(R = n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{16}H_{33}$.)

Luminescent π-conjugated polymers has been the focus of many recent studies aiming efficient organic light-emitting diodes (OLEDs) [6], and various luminescent π-conjugated polymers have been tested as the materials for OLEDs [7]. PPympym is also considered as a candidate for the light-emitting material in OLEDs. However, the earlier shown PPympym with the –NHR group has a strong tendency to form a self-assembled structure, which is disadvantageous for OLED due to providing energy losing pathway(s) by forming excimer-like adduct(s) [8]. On this basis, we have tried to introduce a bulky –NR_2 groups in the side chain of PPympym to prevent the formation of excimer-like adduct(s) originated from the strong tendency to form the self-assembled structure. The research in this line gave PPympym with high molecular weights ($M_n = 19,100–34,000$ with $[\eta]$ values of 2.03–2.18 dl g^{-1}), and the obtained polymer emitted greenish blue light in OLED. Here we report synthesis of new Ppympyms with the bulky –NR_2 and high molecular weights and their light-emitting properties.

2. Experimental part

2.1. Monomer synthesis

2,6-Dichloropyrimido[5,4-*d*]pyrimidine derivatives were obtained in high yields from 2,4,6,8-tetrachloropyrimido[5,4-*d*]pyrimidine. Into a chloroform solution (80 ml) of 2,4,6,8-tetrachloropyrimido[5,4-*d*]pyrimidine (0.60 g, 2.2 mmol) was added dropwise a chloroform solution

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(10 ml) of dihexylamine (2.47 g, 13.3 mmol) at −10 °C. The reaction mixture was stirred for 30 min below 10 °C, followed by removal of chloroform under reduced pressure at room temperature to afford a colorless oil. Further purification by column chromatography on a silica gel column using $CHCl_3$ as an eluent and drying under vacuum gave 2,6-dichloro-4,8-bis(*N*-dihexylamino)pyrimido[5,4-*d*]pyrimidine as a white solid. Yield = 87%, mp = 31–32 °*C*. Anal. Calcd for $C_{30}H_{52}N_6Cl_2$: C, 63.5%; H, 9.2%; N, 14.8%; Cl, 12.5%. Found: C 63.4%; H, 9.1%; N, 14.9%; Cl, 12.7%. ^{1}H NMR ($CDCl_3$, ppm): δ: 4.08 and 3.63 (8H, $N-CH_2$), 1.69 (8H, CH_2), 1.34 (24H, $(CH_2)_3$), 0.90 (t, 12H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ: 158.69 (4,8-C), 153.10 (2,6-C), 135.89 (4^a, 8^a-C), 51.85 (C^1 of hexyl group), 31.57 (C^2), 29.40 (C^3), 26.51 (C^4), 22.63 (C^5), 14.04 (C^6). IR (KBr, cm^{-1}): 2955, 2928, 2856, 1536, 1505, 1419, 1374, 1145, 1069, 908, 740. 2,6-Dichloro-4,8-bis(*N*-didecylamino)pyrimido-[5,4-*d*]pyrimidine was prepared analogously. White solid: Yield = 94%, mp = 51–53 °C. Anal. Calcd for $C_{46}H_{84}N_6Cl_2$: C, 69.7%; H, 10.7%; N, 10.6%; Cl, 9.0%. Found: C 69.5%; H, 10.4%; N, 10.4%; Cl, 9.2%. ^{1}H NMR ($CDCl_3$, ppm): δ: 4.09 and 3.63 (8H, $N-CH_2$), 1.69 (8H, CH_2), 1.34 (16H, $(CH_2)_2$), 1.27 (40H, $(CH_2)_5$), 0.88 (t, 12H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ: 158.69 (4,8-C), 153.10 (2,6-C), 135.89 (4^a, 8^a-C), 51.85 (C^1 of decyl group), 31.90 (C^2), 29.60 (C^3), 29.54 (C^4), 29.36 (C^5 and C^6), 29.32 (C^7), 26.84 (C^8), 22.69 (C^9), 14.11 (C^{10}). IR (KBr, cm^{-1}): 2955, 2922, 2849, 1537, 1506, 1420, 1373, 1142, 1067, 908, 738.

2.2. Polymer synthesis

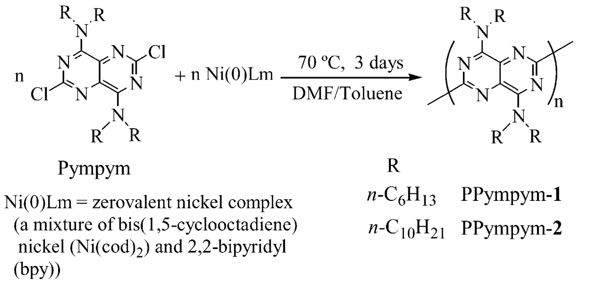
To a DMF/toluene (1/1) solution containing $Ni(cod)_2$ (0.55 g, 2.0 mmol), cod (0.22 g), and bpy (0.31 g, 2.0 mmol) was added 2,6-dichloro-4,8-bis(*N*-dihexylamino)pyrimido[5,4-*d*]pyrimidine (0.57 g, 1.0 mmol) with stirring. After stirring the reaction mixture at 70 °C for 3 days, the reaction mixture was poured into a mixture of NH_4OH(aq) and chloroform. The organic phase was washed with aqueous ammonia (once), a warm aqueous solution of EDTA (ethylenediaminetetraacetic acid) (twice), dil. NH_4OH(aq) (once), and distilled water in this order. The chloroform phase was concentrated and reprecipated into MeOH (twice). The collected yellow solid was dried under vacuum to afford the PPympym-**1** (0.41 g, 0.82 mmol). Yield = 82%. Anal. Calcd for $(C_{30}H_{52}N_6)_n$: C, 72.5%; H, 10.6%; N, 16.9%. Found: C, 72.1%; H, 10.6%; N, 16.9%; Cl, 0.0%. ^{1}H NMR ($CDCl_3$, ppm): δ: 4.65 and 4.05 (8H, $N-CH_2$), 1.70–1.23 (32H, CH_2), 0.78 (12H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ: 159.64 (4,8-C), 153.26 (2,6-C), 136.05 (4^a, 8^a-C), 50.81 (C^1), 31.81 (C^2), 28.90 (C^3), 26.87 (C^4), 22.65 (C^5), and 14.00 (C^6). IR (KBr, cm^{-1}): 2923, 2853, 1521, 1428, 1374, 1064, 861. M_n/M_w (GPC: polystyrene standards in $CHCl_3$) = 19100/92300. $[\eta] = 2.03$ dl g^{-1} (in $CHCl_3$ at 30 °C). Preparation of PPympy-2 was carried out analogously. Yellow solid: Yield = 87%. Anal. Calcd for $(C_{46}H_{84}N_6)_n$: C, 76.6%; H, 11.7%; N, 11.7%. Found: C, 76.2%; H, 11.5%; N, 11.6%; Cl, 0.0%. ^{1}H NMR ($CDCl_3$, ppm): δ: 4.73 and 4.02 (8H, $N-CH_2$), 1.67–1.21 (64H, CH_2), 0.84 (12H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): η:159.74 (4,8-C), 156.35 (2,6-C), 136.13 (4^a, 8^a-C), 50.76 (C^1), 31.90 (C^2), 29.78–29.38 (C^3–C^7), 27.33 (C^8), 22.67 (C^9), and 14.07 (C^{10}). IR (KBr, cm^{-1}): 2925, 2854, 1521, 1427, 1373, 1079, 861. M_n/M_w (GPC: polystyrene standards in $CHCl_3$) = 34000/78400. $[\eta] = 2.18$ dl g^{-1} (in $CHCl_3$ at 30 °C).

2.3. Materials and measurements

N-Dialkylamine (alkyl: hexyl, decyl), 2,2-bipyridyl (bpy), and 1,5-cyclooctadiene (cod) were purchased from Kanto Chemical Co., Inc. Bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, was prepared according to the literature [9]. *N*,*N*-Dimethylformamide (DMF) and toluene were dried, distilled under N_2, and stored under N_2. 2,4,6,8-Tetrachloropyrimido [5,4-*d*]pyrimidine was synthesized according to the literature [4,5]. NMR (^{1}H and ^{13}C) and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO FT/IR-460 spectrometer, respectively. GPC curves were obtained with a Shimadzu liquid chromatography system with a Shodex 80M column and a 6A refractive index detector: eluent = $CHCl_3$. UV–Vis and photoluminescence spectra were reported on a Shimadzu UV-3100 and a Hitachi F-4010 spectrometer, respectively. Double-layer OLED was fabricated by the following procedure. ITO electrode was cleaned with detergent, acetone, and isopropanol in this order. Sequentially washing by UV-ozone method was carried out before deposition of the polymer. A mixture of poly(3,4-ethylenedioxythiophene) PEDOTh and polystyrene sulfonate (BaytronP Al4083) commercialized by Bayer Ltd was used as a hole-injecting layer (HIL) and deposited on the ITO-coated glass from a commercially available aqueous solution; the HIL layer thus obtained was dried at 200 °C. Poly(pyrimido[5,4-*d*]pyrimidine-2,6-diyl) was spin-coated on the top of it from a $CHCl_3$ solution of the polymer. Finally, metal cathodes, calcium (ca. 20 nm) and aluminum (ca. 50 nm), were deposited on top of the polymer layer. The current–voltage-light output characteristics of OLED were measured using a Keithley 2001-type multimeter, and the emission spectrum was measured by a SpectraScan PR650 (Photoresearch Ltd). The OLED data were obtained by Dr T. Ohnishi of Sumitomo Chemical Co. Ltd, to whom the authors express great acknowledgement.

3. Results and discussions

Dehalogenative polycondensation of the dichloro monomers with a zerovalent nickel complex gave the corresponding polymers in high yields (82 and 87%):



(1)

FT-IR and NMR spectra of the polymers were reasonable for the expected structures, and elemental analysis data showed that the polymers did not contain Cl. Table 1 summarizes the results of the polymerization; data for previously reported PPympym-**3** with –NHOct (Oct = octyl) is added for comparison.

The newly obtained Ppympym's were soluble in common organic solvents such as $CHCl_3$ and THF. However, they were not soluble in CH_3OH. PPympym-**1** and **2** showed number-average molecular weight (M_ns) of 19100 ($M_w/M_n = 4.83$) and 34,000 ($M_w/M_n = 2.30$), respectively, in GPC analysis (solvent = $CHCl_3$, vs. polystyrene standards). PPympym-**1** and **2** showed high intrinsic viscosity [η] value of 2.03 and 2.18 dl g^{-1}, respectively, in $CHCl_3$ at 30 °C, although PPympym-**3** prepared previously had M_n of 8800 and [η] value of 0.22 dl g^{-1} in $CHCl_3$ at 30 °C. Increase in the solubility of the monomer and polymer may be the reason for the considerably higher molecular weight. The higher molecular weight is, of course, advantageous for obtaining mechanically strong thin films, and increase of the molecular weight is crucial for polymer OLED's with good performance.

Fig. 1 exhibits the UV–Vis and photoluminescence spectra of the PPympym-**1**. As shown in Fig. 1 and Table 1, the $CHCl_3$ solution of the polymer has the absorption peaks due to the π–π^* transition along the polymer main chain at 429 and 455 nm, which is similar to UV–Vis data of the previously reported PPympym-**3** with octylamino substituents. However, an absorption peak (483 nm) of PPympym-**3** at a longer wavelength, which is considered to originate from the self-assembly of the polymer molecules, is not observed in the UV–Vis spectrum of PPympym-**1**. This is presumably due to the absence of amino-hydrogen atoms, which probably cause the intra- and/or inter-molecular hydrogen-bonding to give the stacked species of the polymer, and/or due to the presence of the bulky $-NR_2$ group. PPympym-**1** film cast on a quartz glass shows the blue-shift of the absorption peak compared with that of the polymer solution (Fig. 1), suggesting that the steric repulsion of bulky dialkylamino groups decreases the coplanarity of the polymer main-chain by the formation of the film. This is in sharp contrast with the data obtained with PPympym-**3** film, which shows a red-shift of the UV–Vis peak from that in solution presumably due to the molecular assembly enhanced in the solid. The shape of the UV–Vis spectrum of PPympym-**2** remained unchanged over a concentration range of 2.6×10^{-5} M (molarity based on the repeating unit) through 8.0×10^{-4} M (0.18 cm cuvette).

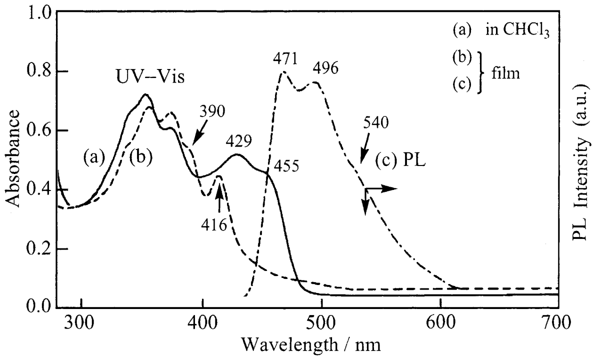


Fig. 1. UV–Vis spectra of PPympym-**1** in (a) $CHCl_3$ (—) and (b) film (– – – –), and (c) photoluminescence spectrum (right) of the polymer film.

Regioregular HT-poly(3-alkylthiophene) [1] and PPympym-**3** show a red-shift of their UV–Vis peaks on addition of CH_3OH (non-solvent) to their $CHCl_3$ (good solvent) solutions, which is accounted for by π-stacking of coplanar molecules in aggregates formed by addition of CH_3OH. On the contrary, PPympym-**2** gives a reverse shift of the UV–Vis peak as shown in Fig. 2. In the formed aggregate of PPympym-**2**, the coplanarity of single molecule of PPympym-**2** seems to decrease due to the presence of bulky NR_2 groups as in the case of film described earlier. These phenomena of PPympym-**2** are in sharp contrast to that of

Table 1
Results of the preparation of Ppympyms and UV–Vis data of the polymers

No.	Polymer[a]	Yield, (%)	$M_n(M_w/M_n)$[b]	Absorption, λ_{max}, (nm) (ε, M^{-1} cm^{-1})	
				$CHCl_3$	Film
1	Ppympym-**1**	82	19100 (4.83)	429 (11200) 455(sh)[c]	390, 416
2	Ppympym-**2**	87	34000 (2.30)	432 (10600) 455(sh)	416 (broad)
3	Ppympym-**3**[d]	90	8800 (1.87)	427 (6900) 452 (9000) 483 (4000)	427, 452, 483

[a] Polymerization was carried out in a mixture of dry DMF/toluene (1/1) at 70 °C for 3 days, unless otherwise noted.
[b] Determination by GPC analysis (eluent = $CHCl_3$ vs. polystyrene standards).
[c] sh = shoulder.
[d] Polymerization condition: in a dry DMF/tolene (4/1) at 60 °C for 48 h.

Table 2
PL data of PPympyms

No.	Polymer	Photoluminescence, λ_{em}, (nm) (λ_{ex}, nm)[a]	
		$CHCl_3$	Film
1	Ppympym-**1**	481, 515, 554(sh), (429, 451)	471, 496, 540(sh), (416)
2	Ppympym-**2**	483, 515, 557(sh), (432, 455)	472, 503, 541(sh), (416)
3	Ppympym-**3**	469, 501, 540, 590, (451) 552, 593, (483)	552, 593, (448, 481)

The wavelength of excitation light (λ_{ex}) is given in parentheses.

[a] sh = shoulder.

PPympym-**3**, and such type of solvatochromism has no precedent to our knowledge.

Table 2 summarizes the photoluminescence (PL) data of the PPympyms in $CHCl_3$ and in film. As shown in Fig. 1 and Table 2, the PL peaks of films of PPympym-**1** and -**2** are shifted by about 10 nm to a shorter wavelength than those of the polymer solution. In addition, PPympym-**1** and -**2** show no PL peak near 590 nm, which is observed with PPympym-**3** and considered to originate from the formation of the excimer-like adducts between photoexcited polymer and the polymer in the ground state. Excitation spectra of PPympym-**1** and -**2** both in $CHCl_3$ and in the solid state agree with UV–Vis spectra of the polymers.

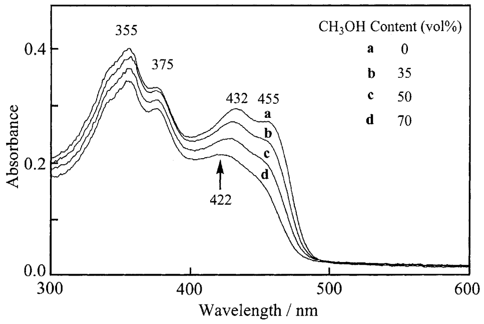


Fig. 2. Changes in UV–Vis spectrum of a $CHCl_3$ solution of PPympym-**2** on addition of CH_3OH at room temperature. [PPympym-**2**] = 2.6×10^{-5} M (monomer unit).

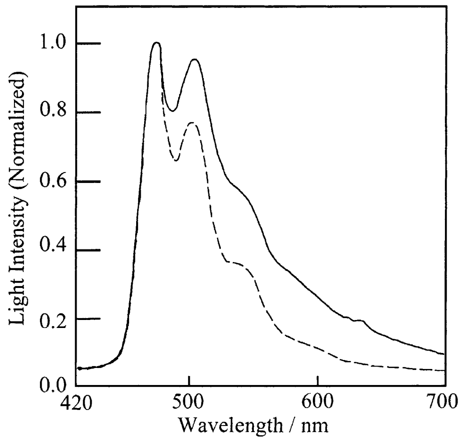


Fig. 3. Photoluminescence (– – – –) and electroluminescence (—) spectra of the film of PPympym-**2**.

By using the newly prepared polymer, OLEDs having a structure of ITO/HIL/PPympym/Ca–Al has been contructed. The double-layer devices prepared by using Ppympyms as a light-emitting layer give greenish-blue light emission. Fig. 3 exhibits PL and EL spectra of the thin film of PPympym-**2**. The EL spectrum of PPympym-**2** with emission peaks at 472 and 504 nm essentially agrees with the PL spectrum of the film of the polymer. PPympym-**1** thin film gives analogous OLED data. Although the turn-on voltage of the OLEDs was relatively high between 29.0 V for HIL/PPympym-**1** and 18.0 V for HIL/PPympym-**2**, use of a mixture of poly(dialkylfluorene) PFO and PPympym in the light-emitting layer decreases the turn-on voltage to 13.0 V for HIL/PPympym-**1** (27 wt%)-PFO and 14.0 V for HIL/PPympym-**2** (23 wt%)-PFO. As described earlier, new π-conjugated polymers with high molecular weights, bulky side chains, and light-emitting properties have been obtained. Further investigation to reveal their electric and optical properties is under progress.

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