Macromolecules **2003,** *36,* 3457−3464

Articles

A Novel Class of Photo- and Electroactive Polymers Containing Oxadiazole and Amine Moieties in a Side Chain

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Received August 29, 2002; Revised Manuscript Received January 22, 2003

ABSTRACT: A new class of photo- and electroactive polymer materials showing an liquid-crystalline (LC) phase were designed and synthesized: four kinds of polymers with both oxadiazole and arylamine moieties as carrier-transporting groups in the side chain. Among them, the polymers with a dimethylamine and a methylcarbazole moiety show LC phases. Furthermore, all the polymers emitted strong blue fluorescence, and their fluorescent quantum yields were over 0.6. The aligned sample of the polymer with the carbazole moiety emitted polarized fluorescence at room temperature. One-layer type electroluminescent (EL) devices were fabricated by using the polymer with a triphenylamine moiety, which exhibited the highest quantum yield (~0.82), and found to emit the EL emission at blue region.

1. Introduction

Electroluminescent (EL) devices based on organic thin layers have attracted much interest because of their possible application as large-area light-emitting displays.[1] Electroluminescence in such systems is generated by recombination of holes and electrons in the emitting layer, which produces excited states in the emitter material. These EL devices, which consist of a doubled layer structure with an organic hole transport layer and a luminescent electron transport layer, show emission with an low-operating voltage. However, the device structure with two organic layers contains an interface between the two layers where only a weak van der Waals force exists; therefore, one-layer-type device may achieve an improvement of structural stability because of the absence of these interfaces.[2]

Liquid crystals (LCs) are promising materials in terms of a unique self-organizing nature and fluidity. Several low molecular-weight LCs containing either hole (benzothiazole) or electron (oxadiazole) conducting groups as mesogens have been synthesized,[3] and some have been investigated as charge transport and, in some cases, EL emission materials. These LCs show high electron and/or hole drift mobilities based on aligned and stacked structures in a smectic (Sm) phase. It was reported that EL devices using these LCs exhibited polarized EL emissions.[3(d)]

We have investigated EL devices using molecularly doped host LCs and evaluated in detail emission behavior of the EL devices.[4] In this system, electronic properties and electrooptical properties were able to be tuned by using various dyes, carrier transport materials and host low molecular-weight LCs.

However, the EL devices consisting of these LCs, like the molecularly doped EL materials using LC matrices and a novel class of LC compounds showing both strong fluorescence and a charge-transporting ability, always require glass cells, so that low molecular-weight LCs are not necessarily promising from the standpoint of material processability.

Currently, polymeric materials are generally expected to be suitable for EL devices because they have good processability and intrinsically high durability. In addition, several one-layer devices with bipolar polymers as well as bipolar dye-dispersed polymers have been reported.[5] The bipolar polymers are classified into two types: p-conjugated polymers[1e,6] and polymers with chromophores.[7] Chromophores are incorporated into the latter polymers on a skeleton and/or on a side chain and the resulting polymers have been shown to be applicable to EL devices as a new class of polymer materials. It was found that there was a very little difference in the driving mechanism between sublimed-dye multilayer and bipolar polymer systems. In addition, from the standpoint of ease of molecular design and synthesis, polymers with chromophores have advantages over fully p-conjugated polymers.

In many areas of material science such as molecular electronics and photonics, the controlled alignment of photoactive chromophores with p-electron conjugation is essential in the application. As decribed above, among

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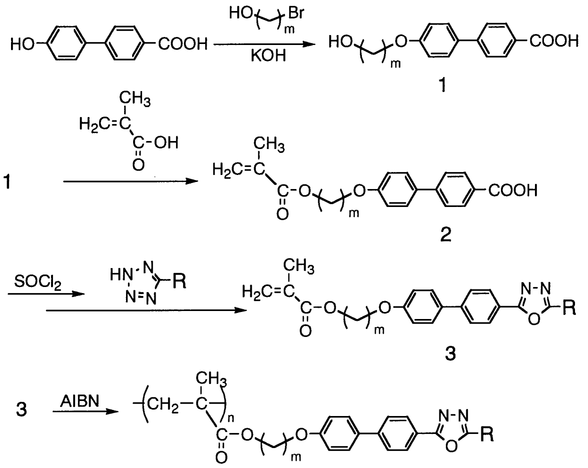
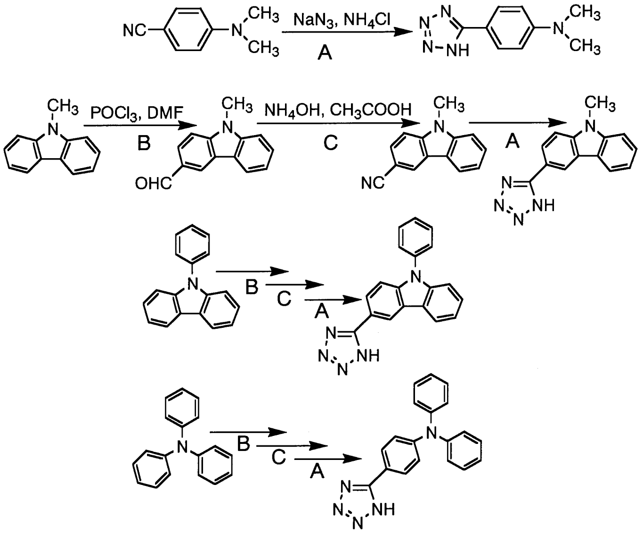
10.1021/ma021406u CCC: $25.00

Scheme 1. Synthetic Route for the Polymers Used in This Work



Scheme 2. Synthetic Route for Various Tetrazole Derivatives Used in This Work



various molecular alignment techniques, cooperative alignment of chromophores in LC media has been intensively studied due to effective alignment and easy processing.[8] However, in a host/guest system, the chromophore content is limited to maintain LC properties of the matrix.

In this work, we report the synthesis of a novel class of polymeric materials which show LC phases and consist of multifunctional mesogens with photo- and electroactive properties. These mesogens are composed of oxadiazole and arylamine moieties as thermally, photochemically, and electrochemically inert moieties.

2. Experiment

2.1. Preparation of Compounds. The oxadiazole monomers in this study were prepared starting from 4-(4-hydroxyphenyl)benzoic acid by a synthetic route shown in Scheme 1, and various tetrazole derivatives were prepared by a procedure shown in Scheme 2 with abbreviations. All regents were purchased from Tokyo Kasei Co. and Aldrich Co. The compounds were identified by ^{1}H NMR, absorption spectroscopy, and elemental analysis.

2.2. Materials. 4-(4-(6-Hydroxyhexyloxy)phenyl)benzoic Acid. 4-(4-(6-Hydroxyhexyloxy)phenyl)benzoic acid (38.6 g, 0.18 mol) was dissolved in a mixture of ethanol (60 mL), potassium hydroxide (27.0 g, 0.48 mol), and water (30 mL). A trace of potassium iodide was added, and the solution was heated and stirred, while 6-bromo-1-hexanol (36.2 g, 0.20 mol) was added slowly. The reaction mixture was heated under reflux for 24 h, and then the solvent was removed by evaporation under reduced pressure. Water (300 mL) was added, and the mixture was made strongly acidic with the addition of hydrochloric acid. The precipitate was isolated and recrystallized from methoxyethanol.

Yield: 22.6 g (72.0 mmol, 40%). Mp: 210−212 °C. ^{1}H NMR (δ, DMSO-d_6): 1.40−1.87 (8H, m), 4.10 (2H, t), 4.22 (2H, t), 7.12 (2H, d), 7.74 (2H, d), 7.81 (2H, d), 8.09 (2H, d). Anal. Calcd for $C_{19}H_{22}O_4$ (314): C, 72.59; H, 7.05. Found: C, 72.70; H, 6.90.

4-(4-(2-Hydroxyethoxy)phenyl)benzoic Acid. The title compound was prepared by the same procedure as 4-(4-(6-hydroxyhexyloxy)phenyl)benzoic acid.

Yield: 20.9 g (81.0 mmol, 45%). Mp: 222−224 °C. ^{1}H NMR (δ, DMSO-d_6): 4.40 (2H, t), 4.61 (2H, t), 7.12 (2H, d), 7.74 (2H, d), 7.81 (2H, d), 8.09 (2H, d). Anal. Calcd for $C_{15}H_{14}O_4$ (258): C, 60.76; H, 5.46. Found: C, 60.99; H, 5.50.

4-(4-(11-Hydroxyundecyloxy)phenyl)benzoic Acid. The title compound was prepared by the same procedure as 4-(4-(6-hydroxyhexyloxy)phenyl)benzoic acid.

Yield: 27.7 g (72.0 mmol, 40%). Mp: 198−200 °C. ^{1}H NMR (δ, DMSO-d_6): 1.40−1.87 (18H, m), 4.12 (2H, t), 4.21 (2H, t), 7.12 (2H, d), 7.74 (2H, d), 7.81 (2H, d), 8.09 (2H, d). Anal. Calcd for $C_{24}H_{32}O_4$ (385): C, 74.97; H, 8.39. Found: C, 75.00; H, 8.41.

4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-carboxylic Acid. A mixture of 4′-(6-hydroxyhexyloxy)biphenyl-4-carboxylic acid (9.40 g, 0.03 mol), methacrylic acid (21.5 g, 0.25 mol), hydroquinone (1.70 g, 0.02 mol), 4-toluenesulfonic acid monohydrate (1.70 g, 0.01 mol), and benzene (200 mL) was heated under reflux in a Dean−Stark apparatus for 24 h. Water was added to the cooled resultant mixture, and then the solvent was removed by evaporation under reduced pressure. The crude product was redissolved in chloroform. The solution was filtered, washed with water and dried over anhydrous magnesium sulfate. The solvent was removed very carefully by evaporation under reduced pressure (maximum water bath temperature was 40 °C) to prevent the formation of oligomers. The crude product was recrystallized from ethanol.

Yield: 4.36 g (11.4 mmol, 38%). Mp: 140−142 °C. ^{1}H NMR (δ, $CDCl_3$): 1.40−1.87 (8H, m), 1.95 (3H, s), 3.99 (2H, t), 4.16 (2H, t), 5.55 (1H, s), 6.10 (1H, s), 6.96 (2H, d), 7.55 (2H, d), 7.60 (2H, d), 8.12 (2H, d). Anal. Calcd for $C_{23}H_{26}O_5$ (382): C, 72.23; H, 6.85. Found: C, 72.30; H, 6.90.

4′-(2-Methacryloyloxyethoxy)biphenyl-4-carboxylic Acid. The title compound was prepared by the same procedure as 4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-carboxylic acid.

Yield: 3.91 g (12.0 mmol, 40%). Mp: 148−150 °C. ^{1}H NMR (δ, $CDCl_3$): 1.96 (3H, s), 4.26 (2H, t), 4.53 (2H, t), 5.60 (1H, s), 6.16 (1H, s), 7.00 (2H, d), 7.57 (2H, d), 7.63 (2H, d), 8.13 (2H, d). Anal. Calcd for $C_{19}H_{18}O_5$ (326): C, 69.93; H, 5.56. Found: C, 70.00; H, 5.61.

4′-(11-Methacryloyloxy-1-undecyloxy)biphenyl-4-carboxylic Acid. The title compound was prepared by the same procedure as 4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-carboxylic acid.

Yield: 4.75 g (10.5 mmol, 35%). Mp: 134−136 °C. ^{1}H NMR (δ, $CDCl_3$): 1.40−1.87 (18H, m), 1.95 (3H, s), 3.99 (2H, t), 4.16 (2H, t), 5.55 (1H, s), 6.10 (1H, s), 6.96 (2H, d), 7.55 (2H, d), 7.60 (2H, d), 8.12 (2H, d). Anal. Calcd for $C_{28}H_{36}O_5$ (453): C, 74.31; H, 8.02. Found: C, 74.42; H, 8.11.

4-Dimethylaminobenzotetrazole (Reaction A). 4-Dimethylaminobenzonitrile (5.00 g, 34 mmol) was dissolved in dry DMF (80 mL), and then sodium azide (36.0 g, 0.55 mol) and ammonium chloride (29.0 g, 0.55 mol) were added to the solution. The solution was stirred and heated under reflux for 10 h. The cooled solution was then added to aqueous hydrochloric acid. The precipitate was collected and washed with water. The recrystallization from toluene/ethyl acetate gave the desired product as a white solid.

Yield: 5.20 g (27.2 mmol, 80%). Mp: 81−83 °C. ^{1}H NMR (δ, DMSO-d_6): 2.99 (s, 6H), 6.85 (d, 2H), 7.83 (d, 2H). Anal. Calcd for $C_9H_{12}N_5$ (189): C, 57.13; H, 5.86; N, 37.01. Found: C, 57.10; H, 5.86; N, 37.00.

3-Formyl-9-methylcarbazole (Reaction B). Phosphoryl chloride (8.00 g, 0.05 mol) was added slowly into DMF (10.0 g, 0.14 mol), which was purged with nitrogen and cooled to 0 °C. The reactant was warmed to room temperature and stirred for 1 h and then cooled again to 0 °C. To this mixture was added *N*-methylcarbazole (5.00 g, 0.03 mol) in 1,2-dichloroethane (13 mL). In 1 h, the reaction temperature was raised to 90 °C and then kept for 8 h. The cooled solution was poured into ice water and extracted with dichloromethane and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane/hexane = 3/1). Recrystallization from hexane/ethanol gave the desired product.

Yield: 7.84 g (22.5 mmol, 75%). Mp: 71−73 °C. ^{1}H NMR (δ, $CDCl_3$): 3.89 (3H, s), 7.30−8.1 (4H, m), 8.05 (1H, d), 8.15 (1H, d), 8.60 (1H, s), 10.10 (1H, s). Anal. Calcd for $C_{14}H_{11}NO$ (209): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.30; H, 5.36; N, 6.74.

3-Formyl-9-phenylcarbazole. The title compound was prepared by the same procedure as 3-formyl-9-methylcarbazole.

Yield: 5.70 g (21.0 mmol, 70%). Mp: 105−107 °C. ^{1}H NMR (δ, $CDCl_3$): 7.30−8.15 (9H, m), 8.40 (1H, d), 8.17 (1H, d), 8.62 (1H, s), 10.5 (1H, s). Anal. Calcd for $C_{19}H_{13}NO$ (271): C, 84.11; H, 4.83; N, 5.16. Found: C, 84.23; H, 4.75; N, 5.14.

3-Cyano-9-methylcarbazole (Reaction C). A mixture of 3-formyl-9-methylcarbazole (3.00 g, 14 mmol), hydroxyamine hydrochloride (1.20 g, 17 mmol), acetic acid (3.00 g, 0.05 mol), pyridine (2.00 g, 25 mmol), and DMF (10 mL) was stirred and heated at 140 °C for 5 h. The crude product was extracted with dichloromethane and washed with water. The product was purified by column chromatography on silica gel (eluent: chloroform/toluene) and recrystallized from hexane/ethanol.

Yield: 2.14 g (10.3 mmol, 74%). Mp: 91−93 °C. ^{1}H NMR (δ, $CDCl_3$): 3.89 (3H, s), 7.25−8.1 (5H, m), 8.15 (1H, d), 8.60 (1H, s). Anal. Calcd for $C_{14}H_{10}N_2$ (206): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.50; H, 5.00; N, 13.50.

3-Cyano-9-phenylcarbazole. The title compound was prepared by the same procedure as 3-cyano-9-methylcarbazole.

Yield: 2.55 g (9.53 mmol, 68%). Mp: 175−177 °C. ^{1}H NMR (δ, $CDCl_3$): 7.26−7.72 (11H, m), 8.18 (1H, d), 8.45 (1H, s). Anal. Calcd for $C_{19}H_{12}N_2$ (268): C, 85.05; H, 4.51; N, 10.44. Found: C, 85.06; H, 4.32; N, 10.62.

3-Tetrazolyl-9-methylcarbazole. A mixture of 3-cyano-9-methylcarbazole (3.00 g, 15 mmol), sodium azide (15.1 g, 0.23 mol), ammonium chloride (12.4 g, 0.23 mol), and dry DMF (110 mL) was stirred and heated at 140 °C for 10 h. The cooled solution was slowly poured into water. The precipitate was collected and washed with water. Recrystallization from toluene/methanol gave the desired product.

Yield: 3.11 g (12.9 mmol, 86%). Mp 264−266 °C. ^{1}H NMR (δ, DMSO-d_6): 3.89 (3H, s), 7.30−8.1 (4H, m), 8.05 (1H, d), 8.15 (1H, d), 8.60 (1H, s). Anal. Calcd for $C_{14}H_{11}N_5$ (249): C, 67.46; H, 4.45; N, 28.09. Found: C, 67.52; H, 4.40; N, 28.08.

3-Tetrazolyl-9-phenylcarbazole. The title compound was synthesized and purified by the same procedure as 3-tetrazolyl-9-methylcarbazole.

Yield: 5.56 g (12.6 mmol, 84%). Mp: 155−157 °C. ^{1}H NMR (δ, DMSO-d_6): 7.30−8.2 (10H, m), 8.09 (1H, d), 8.33 (1H, d), 8.94 (1H, s). Anal. Calcd for $C_{19}H_{13}N_5$ (311): C, 73.30; H, 4.21; N, 22.49. Found: C, 73.14; H, 4.31; N, 22.55.

(4-Tetrazolylphenyl)diphenylamine.[9,10] 4-Tetrazolyltriphenylamine was prepared and purified as reported previously.

Monomer. 2-{4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazole (M6-OXD-MA).[10] 4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-carboxylic acid (3.00 g, 7.85 mmol) was added to thionyl chloride (30 mL) and stirred on heating at 60 °C for 2 h. Excess thionyl chloride was removed by evaporation under reduced pressure, and then the residue was reacted with 4-dimethylaminobenzotetrazole (2.30 g, 12 mmol) in dry pyridine (40 mL) at 135 °C. The cooled solution was poured into water, and the crude product was extracted with dichloromethane and washed with water three times. The product was purified by column chromatography on silica gel (eluent: chloroform/THF = 1/10). Recrystallization from ethanol/toluene gave the desired product.

Yield: 2.51 g (4.80 mmol, 60%). Mp: 115−118 °C. ^{1}H NMR (δ, $CDCl_3$): 1.25−1.89 (8H, m), 1.95 (3H, s), 3.08 (6H, s), 4.00 (2H, t), 4.20 (2H, t), 5.55 (1H, s), 6.11(1H, s), 6.78 (2H, d), 7.04 (2H, d), 7.55 (2H, d), 7.67 (2H, d), 8.05 (2H, d), 8.16 (2H, d). Anal. Calcd for $C_{32}H_{35}N_3O_4$ (523): C, 73.12; H, 6.71; N, 7.99. Found: C, 73.20; H, 6.60; N, 7.93.

2-(4′-Methacryloyloxyethoxybiphenyl-4-yl)-5-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazole (M2-OXD-MA). The title compound was prepared by the same procedure as M6-OXD-MA.

Yield: 2.40 g (5.12 mmol, 64%). Mp: 100−102 °C. ^{1}H NMR (δ, $CDCl_3$): 1.95 (3H, s), 3.05 (6H, s), 4.15 (2H, t), 4.45 (2H, t), 5.55 (1H, s), 6.11(1H, s), 6.68 (2H, d), 6.94 (2H, d), 7.50 (2H, d), 7.62 (2H, d), 7.90 (2H, d), 8.10 (2H, d). Anal. Calcd for $C_{28}H_{27}N_3O_4$ (470): C, 71.63; H, 5.80; N, 8.95. Found: C, 71.57; H, 5.95; N, 8.90.

2-{4′-(11-Methacryloyloxy-1-undecyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-dimethylaminophen)-1,3,4-oxadiazole (M11-OXD-MA). The title compound was prepared by the same procedure as M6-OXD-MA.

Yield: 2.76 g (4.64 mmol, 58%). Mp: 114−116 °C. ^{1}H NMR (δ, $CDCl_3$): 1.25−1.86 (18H, m), 1.95 (3H, s), 3.05 (6H, s), 4.15 (2H, t), 4.45 (2H, t), 5.55 (1H, s), 6.11(1H, s), 6.68 (2H, d), 6.94 (2H, d), 7.50 (2H, d), 7.62 (2H, d), 7.90 (2H, d), 8.10 (2H, d). Anal. Calcd for $C_{37}H_{45}N_3O_4$ (596): C, 74.59; H, 7.61; N, 7.05. Found: C, 74.57; H, 7.64; N, 7.00.

2-{4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-diphenylaminophenyl)-1,3,4-oxadiazole (M6-OXD-PA). 4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-carboxylic acid (3.00 g, 7.85 mmol) was added to thionyl chloride (30 mL) and stirred on heating at 60 °C for 2 h. Excess thionyl chloride was removed under reduced pressure, and then the residue was reacted with (4-tetrazolylphenyl)diphenylamine (4.10 g, 13 mmol) in dry pyridine (40 mL) at 155 °C. The cooled solution was poured into water, and the crude product was extracted with dichloromethane and washed with water three times. The product was purified by column chromatography on silica gel (eluent: chloroform/THF = 1/15). Recrystallization from ethanol/toluene gave the desired product.

Yield: 3.02 g (4.64 mmol, 58%). Mp: 115−118 °C. ^{1}H NMR (δ, $CDCl_3$): 1.25−1.89 (8H, m), 1.98 (3H, s), 4.05 (2H, t), 4.20 (2H, t), 5.56 (1H, s), 6.11(1H, s), 6.97 (2H, d), 7.10−7.40 (12H, m), 7.56 (2H, d), 7.72 (2H, d), 7.95 (2H, d), 8.16 (2H, d). Anal. Calcd for $C_{42}H_{39}N_3O_4$ (650): C, 75.88; H, 6.02; N, 7.17. Found: C, 75.70; H, 6.00; N, 7.23.

2-{4′-(11-Methacryloyloxy-1-undecyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-diphenylaminophenyl)-1,3,4-oxadiazole (M11-OXD-PA). The title compound was prepared by the same procedure as M6-OXD-PA.

Yield: 3.45 g (4.80 mmol, 60%). Mp: 91−93 °C. ^{1}H NMR (δ, $CDCl_3$): 1.25−1.89 (18H, m), 1.98 (3H, s), 4.05 (2H, t), 4.20 (2H, t), 5.56 (1H, s), 6.11(1H, s), 6.97 (2H, d), 7.10−7.40 (12H, m), 7.56 (2H, d), 7.72 (2H, d), 7.95 (2H, d), 8.16 (2H, d). Anal. Calcd for $C_{47}H_{49}N_3O_4$ (720): C, 78.41; H, 6.86; N, 5.84. Found: C, 78.60; H, 6.66; N, 6.00.

2-{4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(3-*N*-phenylcarbazoyl)-1,3,4-oxadiazole (M6-OXD-PCz). The title compound was prepared by the same procedure as M6-OXD-PA.

Yield: 2.85 g (4.40 mmol, 55%). Mp: 118−120 °C. ^{1}H NMR (δ, $CDCl_3$): 1.45−1.89 (8H, m), 1.96 (3H, s), 3.90 (3H, s), 4.04 (2H, t), 4.18 (2H, t), 5.55 (1H, s), 6.11(1H, s), 6.99 (2H, d), 7.33−7.75 (8H, m), 8.25 (4H, m), 8.89 (1H, s). Anal. Calcd for $C_{42}H_{37}N_3O_4$ (648): C, 77.88; H, 5.76; N, 6.49. Found: C, 77.70; H, 5.90; N, 6.32.

2-{4′-(6-Methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(3-*N*-methylcarbazoyl)-1,3,4-oxadiazole (M6-OXD-MCz). The title compound was prepared by the same procedure as M6-OXD-PA.

Yield: 2.91 g (4.96 mmol, 62%). Mp: 140−142 °C. ^{1}H NMR (δ, $CDCl_3$): 1.45−1.89 (8H, m), 1.96 (3H, s), 4.03 (2H, t), 4.18 (2H, t), 5.55 (1H, s), 6.11(1H, s), 6.98 (2H, d), 7.30−7.75 (13H,

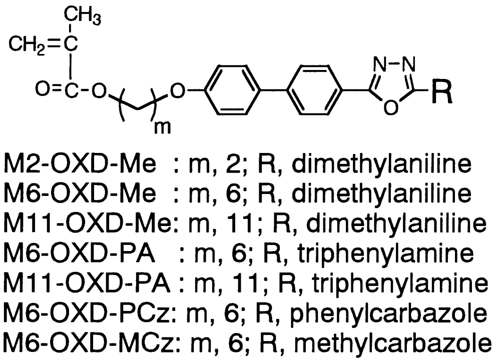


Figure 1. Chemical structures of monomers synthesized in this work.

m), 8.21 (4H, m), 8.91 (1H, s). Anal. Calcd for $C_{37}H_{35}N_3O_4$ (586): C, 75.88; H, 6.02; N, 7.17. Found: C, 75.80; H, 6.00; N, 7.12.

Polymerization. A solution of monomer (1.00 g) and 2,2′-azobis(isobutyronitrile) (1 mol % of monomer) in dry DMF (5 mL) or dry THF (5 mL) was degassed by three freeze−pump−thaw cycles and then sealed off. The mixture was stirred and heated in a sealed tube at 80 °C for 10 h. The cooled solution was poured into 500 mL of hexane with stirring to precipitate the polymer. The polymer obtained was purified by reprecipitation from dichloromethane into hexane three times and dried under vacuum for 48 h.

Yield: (PM2-OXD-MA, 0.45 g, 45%; PM6-OXD-MA, 0.55 g, 55%; PM11-OXD-MA, 0.57 g, 57%; PM6-OXD-PA, 0.61 g, 61%; PM11-OXD-PA, 0.63 g, 63%; PM6-OXD-MCz, 0.38 g, 38%; PM6-OXD-PCz, 0.60 g, 60%).

2.3. LC Phase Behavior. LC behavior and phase transition behavior of the prepared polymers were examined on a polarizing microscope (Olympus model BH−SP) equipped with a hot stage (Mettler EP-82) and by X-ray diffractometry (MAC Science MXP with a thermal controller, model 5301). Thermodynamic properties and T_g were determined with a differential scanning calorimeter (DSC: Seiko I&E SSC 5000) at a heating rate of 10 °C/min. At least four scans were performed for each sample to check reproducibility.

Order parameters (S) were evaluated from the polarized absorption spectra recorded with a UV spectrometer with the aid of a polarizer. Aligned samples for polarized absorption spectroscopy were prepared by annealing the polymers above T_g on a glass plate whose surface was coated with polyimide (PI: 50 nm). The PI surface was mechanically rubbed prior to the spin-coating of polymers on the glass substrate.

2.4. Optical Properties. Absorption spectra were measured with a Jasco V-550 spectrometer and a Shimadzu UV-200 spectrometer. Photoluminescence spectra were taken with a Hitachi F-4000 fluorescence spectrometer. Fluorescent quantum yields (Φ_f) were evaluated spectroscopically using quinine sulfate as a standard at room temperature.

3. Results and Discussion

Figures 1 and 2 show the chemical structures of the monomers and the polymers synthesized in this study. Four kinds of polymers containing an oxadiazole and various arylamine moieties were prepared: poly[2-{4′-(m-methacryloyloxy-1-alkyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazole] is abbreviated as PM*m*-OXD-MA (*m* is alkyl spacer length); similarly, poly[2-{4′-(*m*′-methacryloyloxy-1-alkyloxy)biphenyl-4-yl}-5-(4-*N*,*N*-diphenylaminophenyl)-1,3,4-oxadiazole] as PM*m*′-OXD-PA, and poly[2-{4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(3-*N*-phenylcarbazoyl)-1,3,4-oxadiazole] as PM6-OXD-PCz, and poly[2-{4′-(6-methacryloyloxy-1-hexyloxy)biphenyl-4-yl}-5-(3-*N*-methylcarbazoyl)-1,3,4-oxadiazole] as PM6-OXD-MCz.

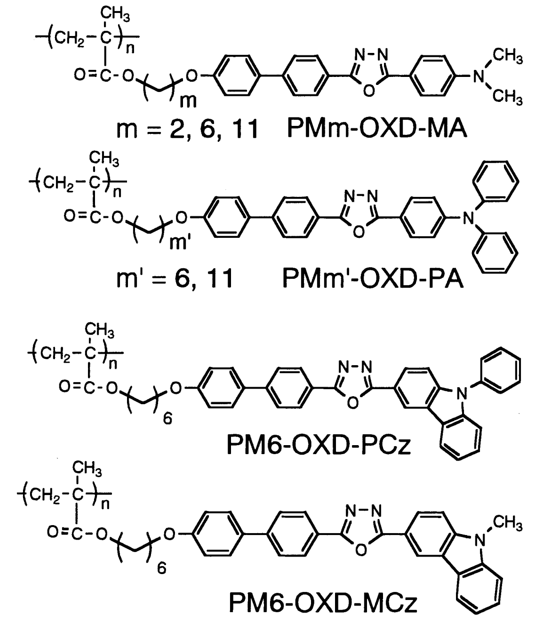


Figure 2. Chemical structures of a new class of polymers prepared in this work.

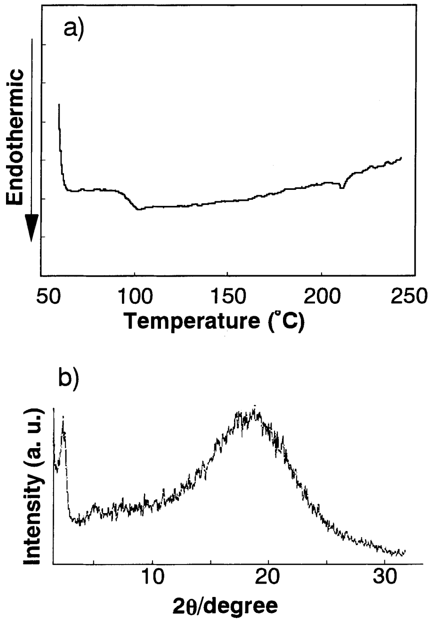


Figure 3. (a) DSC heating thermogram (10 °C/min) of PM6-OXD-MA. (b) X-ray diffraction pattern of PM11-OXD-MA at 150 °C in the SmA phase.

The number-average molecular weights (M_n) were determined by GPC using polystyrenes as standards. The M_n and the molecular weight distribution (M_w/M_n) of each polymer were described as follows. M_n and M_w/M_n: PM2-OXD-MA, 20,000, 1.3; PM6-OXD-MA, 12,000, 1.6; PM11-OXD-MA, 13,000, 1.7; PM6-OXD-PA, 31,000, 1.2; PM11-OXD-PA, 32,000, 1.3; PM6-OXD-PCz, 20,000, 1.4; PM6-OXD-MCz, 9,800, 1.7.

3.1. LC Phase Behavior. In the present work, each polymer was characterized by its LC phase behavior. Figure 3 indicates a DSC thermogram of PM6-OXD-MA on heating. T_g was observed at around 97 °C, and then an endothermic peak due to an LC-isotropic (I) phase transition appeared at around 211 °C. These results indicate that PM6-OXD-MA exhibits a typical DSC curve of a polymer LC showing an LC phase ranging wider than 100 °C.

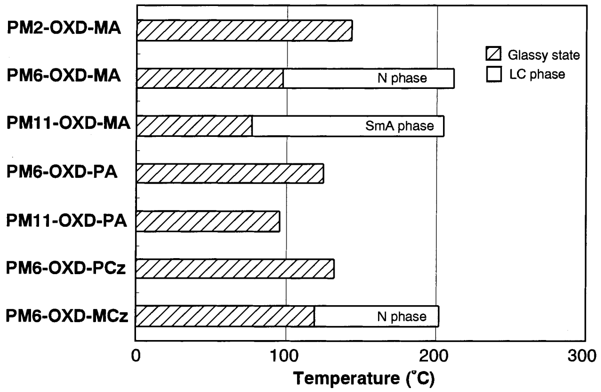


Figure 4. LC behavior of the oxadiazole polymers prepared in this study.

Figure 4 summarizes the results of evaluation of LC phase behavior. In PM*m*-OXD-MA, the LC phase behavior was significantly affected by the alkyl spacer length (*m*). Namely, PM2-OXD-MA with $m = 2$ did not show any LC phase (showed only T_g at 143 °C), while PM6-OXD-MA exhibited a nematic (N) phase (G 97 N 211 I), and PM11-OXD-MA showed a smectic A (SmA) phase (G 77 SmA 205 I). We have performed a definition of LC phase by observation of a polarizing microscope and an X-ray scattering. PM6-OXD-MA showed a Schlieren texture at 150 °C, suggesting that it shows a N phase. On the other hand, in measurement of the X-ray scattering for PM11-OXD-MA at 150 °C, a narrow single peak at around $2\theta = 2.5$ ° and a diffuse halo in a wide angle region were observed, meaning a layer structure (Figure 3b). This result indicates that PM11-OXD-MA shows an SmA phase. It can be seen that PM*m*-OXD-MA showed more highly ordered and wider LC phases as the m increased. In addition, T_g's of PM*m*-OXD-MA were affected by the alkyl spacer length. T_g of PM6-OXD-MA was 97 °C and lower by 46 °C than that of PM2-OXD-MA. Furthermore, T_g of PM11-OXD-MA at 77 °C was lower by 20 °C than that of PM6-OXD-MA. A large drop in T_g of the polymers on increase of the spacer length is commonly observed, and this phenomenon is interpreted as a result of plasticization by the side-chain alkyl moietiy. On the other hand, in PM*m′*-OXD-PA containing triphenylamine as an end group in the side chain, PM6-OXD-PA and PM11-OXD-PA did not exhibit any LC phase regardless of the value of m‘: PM6-OXD-PA and PM11-OXD-PA showed only T_g at 124 and 95 °C, respectively. It seems that steric hindrance between two clusters of benzene rings in the end group of PM*m′*-OXD-PA may prevent the formation of an LC phase. Furthermore, PM6-OXD-PCz also did not exhibit any LC phase; it showed only T_g at 132 °C. These results indicate that the occupied volume of the end group in the side chain is an important factor to show the LC phases. In contrast, it is interesting to note that PM6-OXD-MCz possessing a bent-shaped structure shows an N phase (G 119 N 202 I).

The polymers showing LC phases, namely, PM6-OXD-MA, PM11-OXD-MA and PM6-OXD-MCz, were evaluated on the molecular alignment. Figure 5 shows polarized absorption spectra of PM6-OXD-MA below T_g. The absorbance parallel to the rubbing direction was much higher than that perpendicular to the rubbing direction. This means that the mesogens of PM6-OXD-MA are aligned parallel to the rubbing direction. *S* values of the polymers, which were evaluated by the polarized absorption spectroscopy, are summarized in Table 1. With this geometry of the molecular long axis and the transition moments, *S* can be calculated by the equation $S = (R - 1)/(R + 2)$, where *R* is the dichroic ratio, defined by $R = A_{\parallel}/A_{\perp}$. *S* values of PM6-OXD-MA, PM11-OXD-MA and PM6-OXD-MCz were 0.38, 0.44 and 0.41, respectively. It was found that *S* of PM11-OXD-MA showing an SmA phase was higher than that of PM6-OXD-MA exhibiting an N phase.

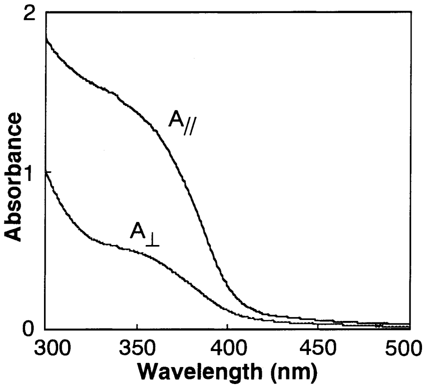


Figure 5. Polarized absorption spectra of PM6-OXD-MA at 23 °C.

Table 1. Dichroic Ratios (*R*) and Order Parameters (*S*) of the Oxadiazole Polymers Synthesized in This Study

polymer	*R*	*S*
PM6-OXD-MA	2.84	0.38
PM11-OXD-MA	3.40	0.44
PM6-OXD-MCz	3.10	0.41

3.2. Optical Properties. Figure 6 shows absorption spectra of the polymers in dichloromethane (10^{-5} M): the extinction coefficients of the entire polymers were 40 000−45 000. Optical properties are very important to evaluate basic characteristics like an energy bandgap of a compound for EL devices.[11−13]

PM2-OXD-MA, PM6-OXD-MA, and PM11-OXD-MA showed absorption maxima at around 345 and 280 nm. PM6-OXD-MA exhibited the same spectrum as PM11-OXD-MA regardless of the alkyl spacer length. Similarly, the absorption spectrum of PM6-OXD-PA was the same as that of PM11-OXD-PA showing absorption maxima at around 366 and 345 nm. On the other hand, PM6-OXD-PCz and PM6-OXD-MCz containing a carbazole moiety as the end group revealed absorption peaks at around 336 nm, shifted to a shorter wavelength region than that of PM6-OXD-MA and PM6-OXD-PA.

Figure 7 displays fluorescence spectra of the polymers in dichloromethane (10^{-6} M). It was found that all the polymers emitted strong blue fluorescence. In PM*m*-OXD-MA, the fluorescence spectrum of PM6-OXD-MA ($\lambda_{ex} = 345$ nm) was the same as that of PM11-OXD-MA ($\lambda_{ex} = 345$ nm) with a peak at around 455 nm. However, PM2-OXD-MA showed a fluorescence maximum at around 460 nm ($\lambda_{ex} = 345$ nm), shifting by 5 nm to longer wavelength than that of PM6-OXD-MA.

With respect to PM*m′*-OXD-PA, PM6-OXD-PA showed a fluorescence peak at around 450 nm and the same spectrum as that of PM11-OXD-PA.

On the other hand, PM6-OXD-MCz and PM6-OXD-PCz, which contained carbazole moieties as an end group in the side chain, showed fluorescence peaks at shorter wavelength than that of PM6-OXD-MA and PM6-OXD-PA. This means that introduction of the carbazole moiety into the side chain affects optical properties, namely, shifts the absorption and fluores-

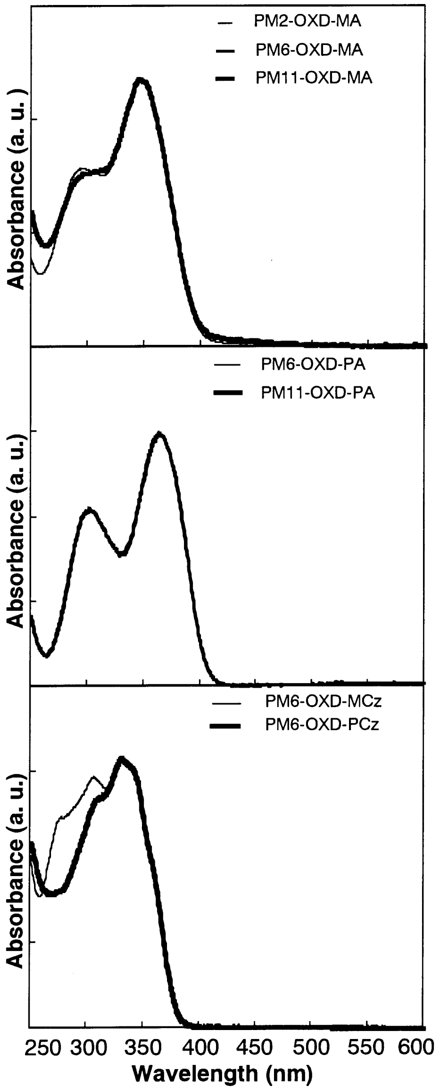


Figure 6. Absorption spectra of the prepared oxadiazole polymers in dichloromethane.

cence peaks to the shorter wavelength. We presumed that the incorporation of carbazole moieties into the side chain leads to the extended π-conjugation, which causes red shifts of the absorption and fluorescence peaks. If π-conjugation were extended by introduction of the carbazole moiety, absorption and fluorescence maxima of both PM6-OXD-PCz and PM6-OXD-MCz would shift to longer wavelength even in solution. However, PM6-OXD-PCz and PM6-OXD-MCz actually showed absorption and fluorescence with a peak shifted to a shorter wavelength region than our expectation. As the carbazole derivatives is assumed to aggregated in solution, at present, a detailed reason for the blue shift in photophysics of the derivatives is under investigation but not clear.

3.3. Quantum Yield of Fluorescence of the Polymer. Φ_f is a very important factor to evaluate a characteristic of compounds for an EL device.[14] The results of Φ_f measurements of PM6-OXD-MA, PM6-OXD-PA, PM6-OXD-PCz, and PM6-OXD-MCz are shown in Table 2. It was found that all the samples exhibited high yields (over 0.6). Especially, PM6-OXD-PA showed the highest Φ_f value (0.82), and the Φ_f value of PM6-OXD-MCz showing an LC phase was 0.72.

3.4. Polarized Fluorescence. Aligned films of PM6-OXD-MCz were prepared by spin-coating from solution on a glass substrate whose surface was coated with mechanically rubbed polyimide films. The homogeneously aligned films were obtained after annealing in the N phase at 145 °C for 2 h.

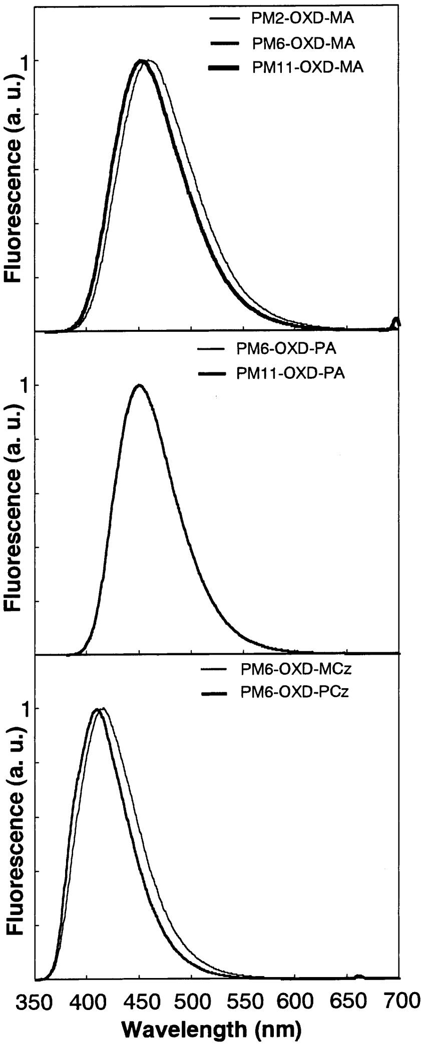


Figure 7. Fluorescence spectra of the prepared oxadiazole polymers in dichloromethane.

Table 2. Photoluminescent Quantum Yields of the Polymers in Dichloromethane

polymer	Φ_f[a]	λ_{ex} (nm)[b]	liquid crystal[c]
PM6-OXD-MA	0.60	345	○
PM6-OXD-PA	0.82	364	
PM6-OXD-PCz	0.73	336	
PM6-OXD-MCz	0.72	336	○

[a] Quantum yields. [b] Excitation wavelength. [c] Open circle: showed an LC phase.

Figure 8 shows polarized fluorescence spectra of an aligned film of PM6-OXD-MCz. In this case, the excitation wavelength was 336 nm with unpolarized light. It was found that the intensity of fluorescence polarized parallel to the rubbing direction was much higher than that polarized perpendicular to the rubbing direction. A dichroic ratio ($I_{\parallel}/I_{\perp}$) was estimated as 3.5 at 430 nm.

3.5. EL Emission of PM6-OXD-PA. A one-layer type EL device using PM6-OXD-PA, which showed the highest quantum yield, was fabricated. The structure of the EL device is shown in Figure 9. A patterned ITO-coated glass substrate was used as a transparent anode. On the ITO anode, PM6-OXD-PA film was spin-coated from

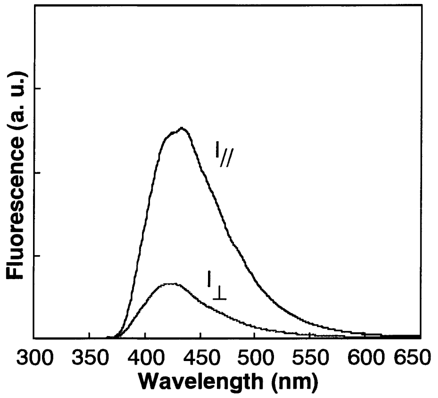


Figure 8. Polarized fluorescence spectra of PM6-OXD-MCz. $I_{\parallel}$, fluorescence polarized parallel to the rubbing direction; $I_{\perp}$, fluorescence polarized perpendicular to the rubbing direction.

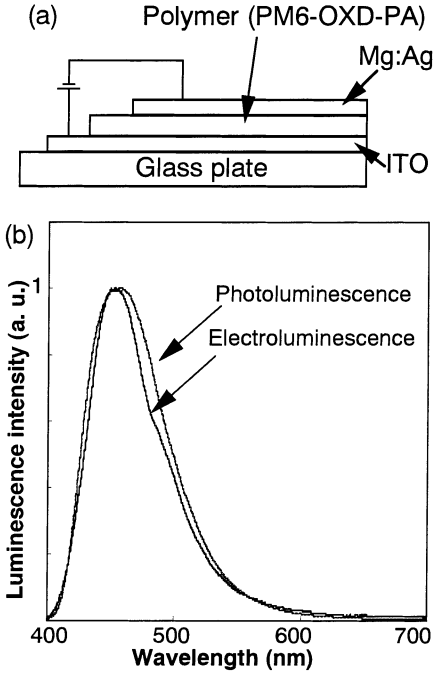


Figure 9. Configuration of EL devices using PM6-OXD-PA (a) and photoluminescence and electroluminescence spectra of PM6-OXD-PA (b).

a 1 wt % dichloromethane solution, and the polymer film was dried and annealed at 140 °C for 1 h. The thickness of the polymer film was 100 nm. Furthermore, a magnesium/silver (10/1) alloy cathode, 100 nm in thickness, was directly deposited on top of the polymer film under vacuum (6×10^{-6} Pa). The emitting area of the EL devices was 2×2 mm^2.

Figure 9 compares the EL spectrum from the EL device with the photoluminescence spectrum of the film of PM6-OXD-PA. In the EL device, the bright blue EL emission was observed. The EL peak was found to be located at 453 nm, which corresponded well to the photoluminescence peak. The shape of the EL spectrum was almost the same as that of the photoluminescence spectrum, except for a small difference at the longer wavelength region. It is clear that charge recombination and emission occur on the chromophore of PM6-OXD-PA.

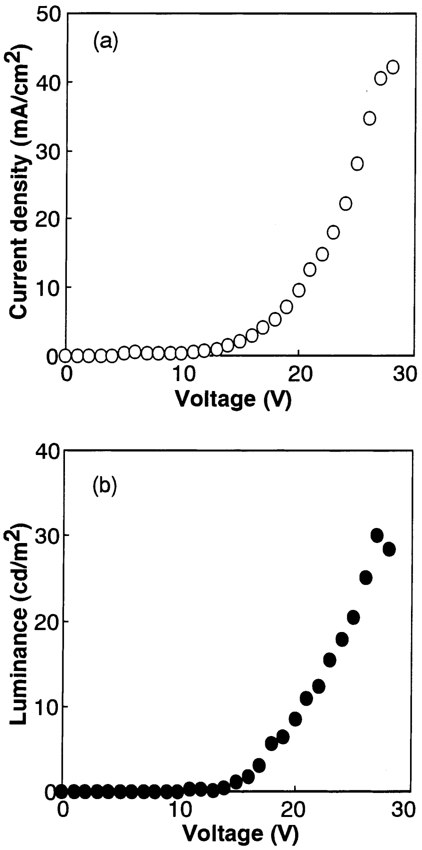


Figure 10. Current density–voltage characteristic of the EL device consisting of PM6-OXD-PA (a) and luminance–voltage characteristic of the EL device (b).

The current density–voltage relationship in the EL devices is shown in Figure 10 a. The EL device had a turn-on voltage of the current density at 10 V. The current density increased with the applied voltage and a maximum current density of 43 mA/cm^2 was obtained at 28 V.

In Figure 10b, luminance–voltage characteristic of the EL device is shown. The EL device had a turn-on voltage of luminance at 10 V as well as the current density. Compared with other EL polymers with an active moiety in a side chain,[15] a single layered EL devices consisting of PM6-OXD-PA showed a lower turn on voltage. The luminance intensity increased with increasing the applied voltage and a maximum luminance of 30 cd/m^2 was obtained at 27 V.

4. Conclusion

A novel class of functional polymers were designed and synthesized. Among the materials, the polymers containing a dimethylamine moiety as an end group in the side chain and the polymer introducing a carbazole unit as an end group in the side chain showed LC phases: PM6-OXD-MA and PM11-OXD-MA showed an N phase and an SmA phase, respectively, and PM6-OXD-MCz exhibited an N phase. All the polymers emitted strong blue fluorescence and exhibited high quantum yields (over 0.6). In addition, PM6-OXD-MCz showed the fluorescence anisotropy, and the one-layer type EL device using PM6-OXD-PA, which exhibited the highest quantum yield of fluorescence, emitted EL emission at a blue region. These compounds, therefore, are potential for multifunctional LC materials for many elecroactive devices.

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