Green light-emitting diodes from poly(2-dimethyloctylsilyl-1,4-phenylenevinylene)

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A novel silyl-substituted solvent processable poly(1,4-phenylenevinylene) (PPV) derivative, poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV) is synthesized by the dehydrohalogenation route from 2-dimethyloctylsilyl-1,4-bis(bromomethyl)benzene, and the light-emitting properties of the polymer are studied; single layer electroluminescent devices (ITO/polymer/Ca or Al) exhibit an emission maximum at 520 nm with internal quantum efficiency in the range 0.2–0.3%.

Light-emitting polymers have been extensively investigated in recent years since the Cambridge group first reported a green light-emitting diode (LED) using poly(1,4-phenylenevinylene) (PPV) as an emitting layer.[1–4] Organic polymer LEDs have many advantages for the development of a large-area visible light-emitting display, because of the good processability, low operation voltage, fast response time and colour tunability over the full visible range by control of the HOMO–LUMO bandgap of the emissive layer. PPV has been most widely used as the emissive layer for the light-emitting diodes, and has been prepared through a thermal elimination process from a water-[5] or organic-soluble precursor polymer.[6–8] Several organic solvent soluble PPV derivatives have been developed in order to improve processability.[9–11] Recently, Zhang *et al.* reported the improved quantum efficiency in green polymer light-emitting diodes with a silyl-substituted soluble PPV derivative, poly(2-cholestanoxy-5-thexylsilyl-1,4-phenylenevinylene) (CS-PPV).[11] They reported[12] that CS-PPV showed high quantum efficiency with an air-stable aluminium electrode by adding an electron transporting molecular dopant, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD).[13,14]

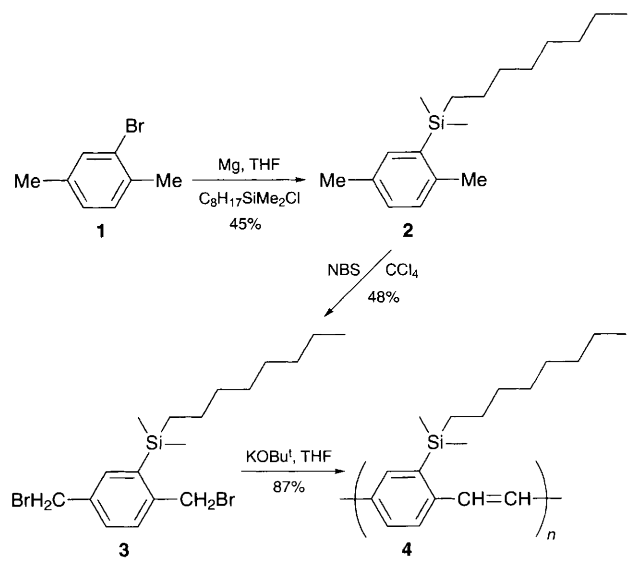
The effects of silicon substitution on the luminescence properties are of interest in the field of polymer LEDs, and here we report the synthesis of a new silyl-substituted soluble PPV derivative, poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV). Single layer electroluminescent (EL) devices have been fabricated using this polymer as the emissive layer. The synthetic route is outlined in Scheme 1. Silylation of the Grignard reagent derived from **1** afforded the silyl derivative **2** which after radical bromination gave the dibromo-compound **3**.† Dehydrohalogenation condensation polymerization afforded DMOS-PPV **4**.[15,16]

DMOS-PPV **4** is completely soluble in common organic solvents such as chloroform, tetrahydrofuran and toluene without evidence of gel formation.

Fig. 1 shows the UV–VIS, photoluminescence (PL) and EL spectra of the DMOS-PPV film. DMOS-PPV **4** shows a slightly narrower absorption band compared with PPV. The absorption maximum and edge of the DMOS-PPV are at *ca.* 414 and 500 nm, respectively, at room temperature. These positions are blue-shifted compared with those of the unsubstituted PPV (420 and 530 nm, respectively), presumably owing to the steric effect of the bulky dimethyloctylsilyl group.

DMOS-PPV **4** shows an emission maximum at *ca.* 520 nm which corresponds to the green region. The absolute photoluminescence quantum efficiency for a solid film of DMOS-PPV was 60%. By comparison, the reported PL efficiencies of PPV and MEH-PPV are 27 and 15%, respectively.[17]

Fig. 2 shows the current density–electric field characteristics measured for a typical ITO/DMOS-PPV/Al device with film thickness of 700 Å. The forward current density increases with increasing forward bias field and the curve shows typical diode



Scheme 1

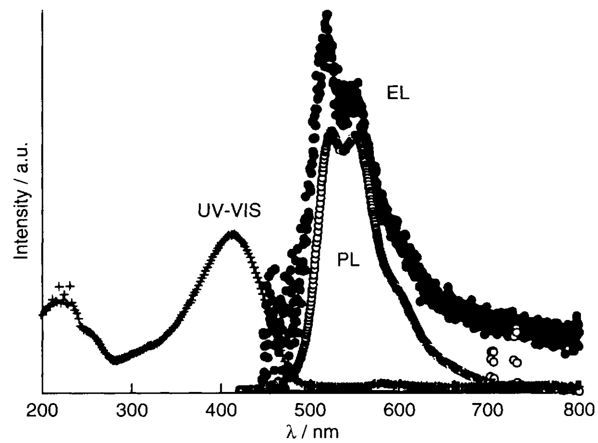


Fig. 1 UV–VIS (crosses), PL (open circles) of DMOS-PPV film and EL (solid circles) of the ITO/DMOS-PPV/Al device

characteristics. The voltage dependence of emission intensity from the device shows that light emission becomes observable at a bias of about 15 V at a current density of 0.93 mA cm^{-2}. The devices showed reproducible internal quantum efficiencies of 0.2% (*ca.* 0.05% external efficiency).‡

Fig. 3 shows the current density–field characteristics of an ITO/DMOS/Ca device (700 Å thickness). The threshold voltage of the device was about 11 V at a current density of 1.8 mA cm^{-2}. The measured maximum internal quantum efficiency of the diode was 0.3% (*ca.* 0.1% external efficiency). These values compare favourably with the efficiency of the single layer green polymer LED reported by Son *et al.*[8]

Recently we have fabricated multilayer EL devices with DMOS-PPV and various charge-transporting materials, such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) or poly(aromatic oxadiazole)s. These devices showed highly improved quantum efficiencies using an aluminium cathode.

The DMOS-PPV film has good processability and the high quantum efficiency may make it a good candidate for application in polymer LEDs.

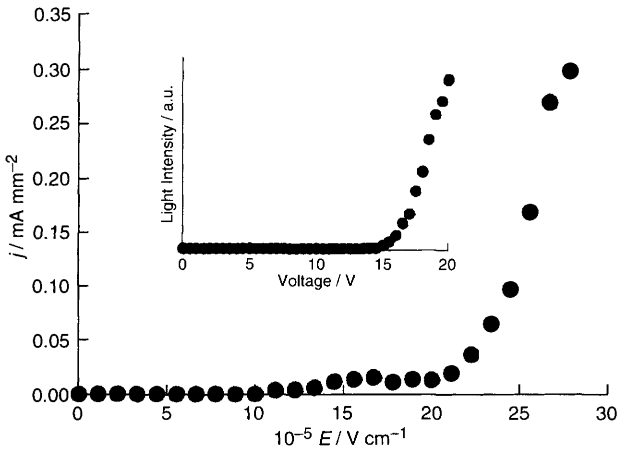


Fig. 2 Current density–electric field and light intensity–voltage (inset) characteristics of ITO/DMOS-PPV/Al device

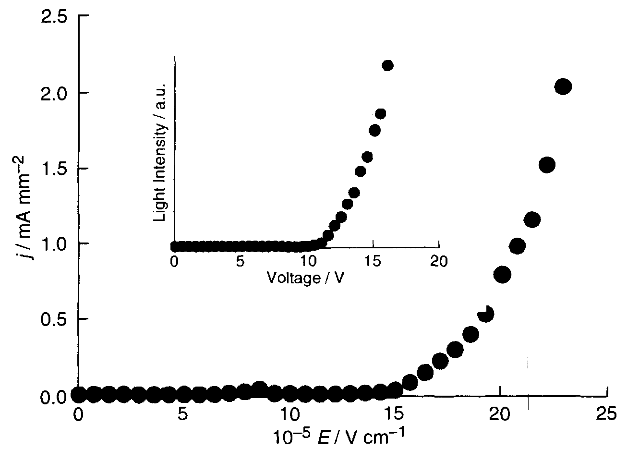


Fig. 3 Current density–electric field and light intensity–voltage (inset) characteristics of ITO/DMOS-PPV/Ca device

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Footnotes

† *Selected spectroscopic data.* **2**, ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.28 (1 H, s), 7.09 (2 H, s), 2.43 (3 H, s), 2.34 (3 H, s), 1.41–1.14 (12 H, m), 0.97–0.75 (5 H, m), 0.33 (6 H, s); **3**, ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.48 (1 H, s), 7.43 (2 H, s), 4.61 (2 H, s), 4.48 (2 H, s), 1.43–1.19 (12 H, m), 0.99–0.81 (5 H, m), 0.42 (6 H, s); DMOS-PPV **4**, GPC (polystyrene standard) showed a M_w of 1.1 × 10^6 and polydispersity index of 7.2. (Found: C, 77.5; H, 10.05. Calc. C, 79.34; H, 10.36%). FTIR (NaCl) ν_{max}/cm^{-1} 2955, 2922, 2853, 1729, 1468, 1377, 1251, 1137, 1066, 961, 836.

‡ The internal efficiency is a factor of $2n^2$ larger than the external efficiency where n is the refractive index of the emissive layer.[18]

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