Green-Blue Photoluminescence from a Novel Silicon-Containing Alternating Copolymer

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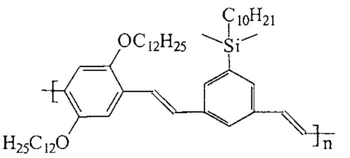
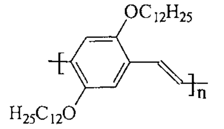
A novel silicon-containing copolymer with an alternating structure, poly[(5-decyldimethylsilyl-1,3-phenylenevinylene)-*alt*-(2,5-didodecyloxy-1,4-phenylenevinylene)], is synthesized through the Wittig reaction. The polymer is a promising green-blue emissive material for light-emitting device application due to its good solubility, high thermal stability, and intense photoluminescence.



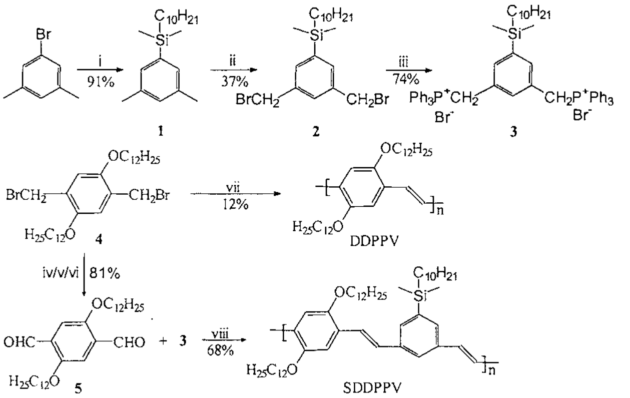
SDDPPV



DDPPV

Luminescent conjugated polymers have attracted much attention since the first observation of electroluminescence in a light-emitting diode (LED) fabricated from poly(*p*-phenylenevinylene).[1] Conjugated polymers demonstrate many advantages as materials for LED applications. They can be easily fabricated as smooth and large-area emission layer through simple spin casting technique.[2] The emission color can be tuned from red to blue by adjusting the chemical structures.[3] Short wavelength light generated from emissive polymers is much promising for display technology because so far inorganic semiconductors are proven to be difficult for large-area flat panel applications. Several polymer systems have been developed for blue and green light emission.[4-9] Blue light emission is obtained from wide band gap materials, which can be tailored by controlling the π electron delocalization along the polymer backbone. One approach is to incorporate non-conjugated segments into the backbone so as to shorten the conjugation length for the enlargement of band gap.[6] However, charge transporting in the conjugation-interrupted polymer system will be greatly reduced due to the existence of non-conjugation segments along the polymer backbone. The other is to limit the effective conjugation of π electrons along the conjugated main chain either by rigid linkage of two bulky adjacent units, *e.g.*, PPPs,[4] ladder PPPs[5] and PFs[7] or by introducing some content of *meta*-linkage of the phenylene ring in PPV derivatives.[9] PPV derivatives are a class of well established materials for PLED applications because of their good processability, thermostability, high PL and EL efficiencies and ease of synthesis. In this communication, we present the synthesis and characterization of a novel high efficient green-blue photoluminescent copolymer poly[(5-decyldimethylsilyl-1,3-phenylenevinylene)-*alt*-(2,5-didodecyloxy-1,4-phenylenevinylene)] (SDDPPV) with an alternating structure, in which one block is based on *para*-phenylenevinylene and the other unit is linked through *meta*-position of the phenylene ring incorporated with a silyl group. The introduction of a silyl group into the polymer system is with the aim of further improving the luminescent efficiency, solubility, and film-forming ability.[10-12] For the sake of comparison, a homopolymer poly(2,5-didodecyloxy-1,4-phenylenevinylene) (DDPPV) has also been synthesized.

The synthetic routes for SDDPPV and DDPPV are outlined in Scheme 1. 5-decyldimethylsilyl-*m*-xylene (**1**) was obtained through the coupling of the Grignard reagent derived from 5-bromo-*m*-xylene and decyldimethylsilyl chloride. After the radical bromination, compound **2** was converted to triphenyl phosphonium salt to afford a monomer **3**. 2,5-didodecyloxy-1,4-bisbromomethyl-benzene (**4**) was prepared from 1,4-didodecyloxybenzene by bromomethylation. The monomer **4** was converted to diformyl compound by esterification and hydrolysis, then oxidized by pyridinium chlorochromate (PCC) to afford another monomer **5** with a very high yield and high purity. Monomers **3** and **5** were polymerized through the Wittig reaction.[13] The obtained polymer is a green solid after twice precipitation of its chloroform solution in methanol, which is fully soluble in common organic solvents such as chloroform, THF, dichloromethane, toluene, and xylene.



Scheme 1. The synthetic routes for SDDPPV and DDPPV. Reagents and conditions: i) Mg/THF/n-$C_{10}H_{21}(CH_3)_2SiCl$; ii) NBS/benzene/BPO/hν; iii) PPh_3/DMF; iv) NaI/NaOAc/DMF; v) NaOH/EtOH/H_2O; vi) PCC/CH_2Cl_2; vii) KO^{t}Bu/xylene; viii) EtOH/$CHCl_3$/EtONa.

The chloroform solution of the polymer shows good film forming ability and the film formed by spin-coating onto clean ITO glass substrate illustrates smooth surface and homogeneous morphology observed by atomic force microscopy (AFM). It is well known that a smooth film is helpful to form a low barrier interface with electrode when fabricated into devices and can improve the EL efficiencies.[11] The PL efficiency of the film samples is 65% which is higher than that of PPP derivatives[4] and poly(alkylfluorene).[14]

The reference polymer DDPPV was synthesized by dehydrohalogenation reaction of monomer **4** and potassium *tert*-butoxide using xylene as solvent. In this step, the reaction conditions such as the amount of base used, reaction time, temperature, and the choice of solvent should be carefully controlled to prevent gel formation. Even so, most of DDPPV is insoluble and the yield of the soluble part is very low. This is one of the reasons that we introduce a silyl group as the pendant to the copolymer to improve the solubility. The soluble part of DDPPV in chloroform was used for a comparison study.

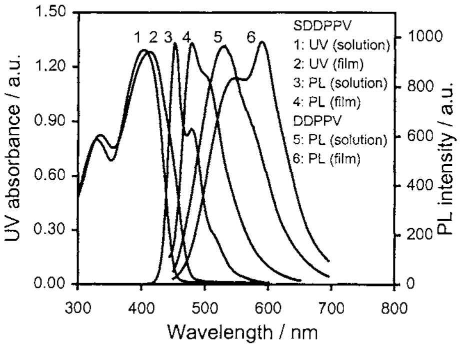


Figure 1. The UV-Vis absorption and photoluminescence spectra of the solution and film samples of SDDPPV and DDPPV.

Figure 1 shows the UV-Vis absorption and photoluminescence spectra of SDDPPV and DDPPV. The UV-Vis absorption spectra for SDDPPV film and solution samples are quite similar. The maximum peaks of the absorption take place at 412 and 403 nm and the side peaks at 335 and 330 nm, respectively. The side peaks could be assigned to the π-π^* transition of monomer repeat unit and the main peaks are due to the delocalized π electrons transition along the backbone. The absorption edge is at 480 nm, which corresponds to 2.6 eV of band gap. The photoluminescence spectra for solution and film samples display some difference. The main peak for the solution sample is at 452 nm with a clear resolved medium side peak at 479 nm, which is associated with the vibronic coupling of the excitons. While the main peak for the film sample takes place at 479 with a shoulder at 502 nm, which means the emission area lies in the region of green-blue. The PL spectra for DDPPV are quite different from those of SDDPPV. The spectrum for the solution sample is broadened and the maximum emission is at 530 nm, while the spectra for the film one shows a main peak at 590 nm with a shoulder at 547 nm, corresponding to an orange emission. Compared the PL spectra of DDPPV to those of SDDPPV, it can be seen that the introduction of *meta*-linkage of the phenylene unit into the polymer backbone can effectively lower the conjugation of the π electrons along the main chain, which will lead to a strong blue-shift of the emission spectra. It is also noted that the emission peak of SDDPPV is much narrower than that of DDPPV. The evaluation of EL performance of the polymer is in progress.

In summary, a novel silicon-containing solution processable copolymer with high efficient luminescence, based on a *para*-phenylenevinylene and *meta*-phenylenevinylene alternating structure has been successfully synthesized through the Wittig reaction. The *meta*-linkage along the polymer backbone can effectively lower the π electron conjugation, therefore, lead to the photoluminescence spectra strongly blue shift and lie in the green-blue region of the emission spectra. The solubility and film-forming ability of the copolymer are quite good due to introducing a silyl group as one of the side chains in the copolymer. The polymer may be a promising greenish-blue emissive material for polymer LED application.

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13 Selected spectroscopic data: **3**, ^{1}H NMR ($CDCl_3$, ppm) δ -0.21 (6H, s), 0.22 (2H, t), 0.87 (3H, t), 1.12-1.25 (16H, m), 5.22 (4H, d), 6.85 (2H, s), 7.11 (1H, s), 7.58-7.78 (30H, m); **5**, ^{1}H NMR (CDCl$_3$, ppm) δ 0.88 (6H, t), 1.27-1.54 (36H, m), 1.81 (4H, m), 3.98 (4H, t), 4.52 (4H, s), 6.85 (2H, s); SDDPPV, ^{1}H NMR (CDCl$_3$, ppm) δ 0.35 (6H, s), 0.88 (17H, m), 1.24-1.60 (46H, m), 1.91 (4H, m), 4.10 (4H, m), 6.65-6.72 (2H, m), 7.12-7.24 (3H, m), 7.33-7.58 (4H, m); Found: C, 80.78; H, 10.78%. Anal. Calcd for $(C_{52}H_{86}O_2Si)_n$: C, 81.04; H, 11.17%. FT-IR (KBr) ν_{max}/cm^{-1} 3057, 2926, 2855, 1583, 1495, 1470, 1421, 1246, 1194, 1132, 1024, 959, 837, 810, 715. Gel permeation chromatography (GPC) measurement using THF as eluent and polystyrene as standard indicated M_n = 20400 with polydispersity index of 1.43.

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