Ultraviolet-emitting conjugated polymer poly(9,9′-alkyl-3,6-silafluorene) with a wide band gap of 4.0 eV†

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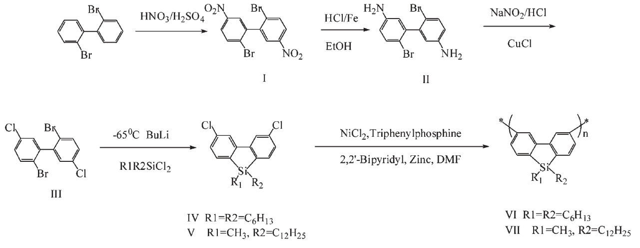
An ultraviolet-emitting conjugated polymer, poly(9,9′-alkyl-3,6-silafluorene) with a wide band gap of 4.0 eV, has been synthesized and characterized.

Violet and ultraviolet (UV) light-emitting polymers have attracted great interest because they can be used to generate emission over the whole visible range and white light emission either by the irradiation of luminescent dyes or *via* energy transfer from host materials to emissive dopants, especially phosphorescent dyes. However, it is difficult to realize UV light emission with π-conjugated polymers. The majority of UV-luminescent polymers reported so far in the scientific literature are non-conjugated polymers with a pendant UV chromophore.[1,2] Some σ-conjugated polysilanes[3,4] are reported as UV-emitting polymers. As for conjugated polymers, electron-deficient moieties such as oxadiazole,[5] pyridine[6] and terpyridine[7] were introduced into the main chain in order to increase the band gap. An alternative way to obtain UV emission from a conjugated copolymer is to decrease the coplanarity of arylene units[8–10] or to introduce meta linkages into the polymer backbones.[8,11] The shortest wavelength achieved so far from an electroluminescent device with a conjugated polymer has been reported by Zhang *et al.*[8] A conjugated polymer with a band gap of 3.26 eV consisting of alternating dihexylfluorene and rigidly twisted biphenyl units exhibits a photoluminescent (PL) emission with a peak at 368 nm and an electroluminescent emission with a peak at 395 nm.[8]

In this paper we report a novel conjugated polymer, poly(9,9′-alkyl-3,6-silafluorene) with a wide band gap of 4.0 eV. Although a homopolymer, poly(2,7-silafluorene) has been reported by a Cambridge group recently,[12] poly(2,7-silafluorene) has a band gap of 2.93 eV with an emission peak at around 420 nm in film, which is similar to its carbon analog polyfluorene[13] or its nitrogen analog polycarbazole.[14,15] Silafluorene is of great interest since it contains a highly emissive unit, silole[16] with a structure similar to fluorene with 9-carbon replaced by Si in fluorene. Silafluorene has been studied since the 1950s,[17] and derivatives of it such as spirosilabifluorenes[18] were reported recently. However, the attempt to synthesize poly(9,9′-alkyl-3,6-silafluorene) by an ordinary method *via* the coupling of dibromofluorene and dibromocarbazole failed because the silole ring in the silafluorene underwent a ring-opening reaction during bromination with Br_2, *N*-bromosuccinimide and CCl_3Br and during polymerization in the presence of an oxidant, such as $FeCl_3$. We designed a new synthetic route to synthesize poly(3,6-silafluorene) to solve this problem (Scheme 1). The starting monomer, 3,6-dichloro-9,9′-alkylsilafluorene (**IV**, **V**) was synthesized from 2,2′-dibromobiphenyl *via* 2,2′-dibromo-5,5′-dichlorobiphenyl (**III**) following the procedure described in the Supporting Information.† The advantage of using 2,2′-dibromo-5,5′-dichlorobiphenyl is that chloride groups do not react with BuLi in the ring-closing reactions, so an aryl–aryl bond can be formed by nickel-catalyzed reaction of the resulting 3,6-dichloro-9,9′-alkylsilafluorene in the presence of triphenylphosphine, zinc, 2,2′-bipyridine, and $NiCl_2$.[19] Details of the synthesis and NMR characterization (Figs. S1–S12†) can be found in the SI.

The molecular weight of **VI** is estimated, by gel permeation chromatography (GPC) against polystyrene standards, at around 16000/10000 (M_w/M_n) with a polydispersity of around 1.6. All these polymers can be processed by spin coating from common organic solvents, such as toluene, THF and chloroform, to form thin polymer films. The thermal properties of the polymers were evaluated by TGA (thermogravimetric analysis) and DSC (Differential Scanning Calorimetry) measurements (Fig. S13 and Fig. S14†). TGA reveals excellent thermal stability of poly(3,6-silafluorene) at a decomposition temperature (5% weight loss) of 442 °C for PSFC6C6 and 425 °C for PSFC1C12, which is much higher than that of poly(2,7-fluorene) (380 °C).[20] Poly(3,6-silafluorene) in darkness and under room light illumination shows oxidative stability similar to polyfluorenes (Fig. S15 and Fig. S16†). For DSC scans, poly(9,9′-alkyl-3,6-silafluorene) showed similar glass transition temperatures: 83 °C for **VI** and 58 °C for **VII** (Fig. S14†), which is close to T_g = 75 °C reported for poly(9,9′-dioctyl-2,7-fluorene).[20] This indicates that the replacement of carbon in position 9 of polyfluorene by silicon does not change the polymer chain stiffness.

Fig. 1 shows absorption and photoluminescence spectra of **VI** and **VII**. These polymers exhibit an identical absorption peak at 250–300 nm and an identical absorption edge of around 310 nm in thin films as well as in dilute solutions. The absorption maximum



Scheme 1 Synthesis route of poly(3,6-silafluorene).

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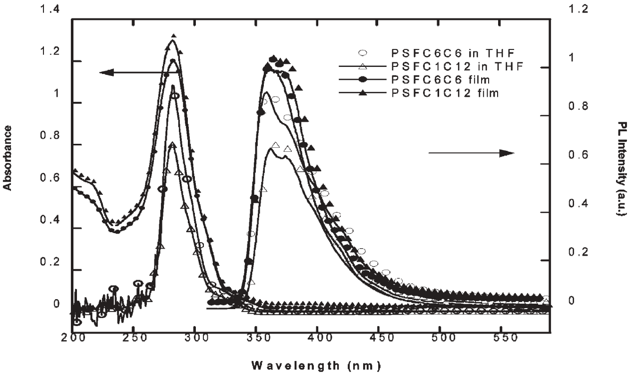

Fig. 1 UV-vis and PL spectra of PSFC6C6 (**VI**) and PSFC1C12 (**VII**). **VI** in THF 0.012% (mg mL^{-1}) (open circles), **VI** film (solid circles), **VII** in THF 0.008% (mg mL^{-1}) (open triangles), **VII** film (solid triangles).

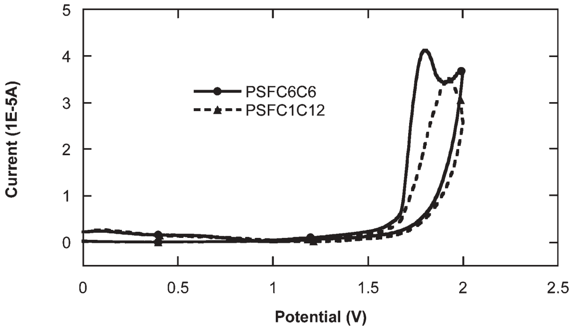

Fig. 2 Cyclic voltammograms of PSFC6C6 (**VI**) and PSFC1C12 (**VII**) in 0.1 M Bu_4NPF_6 / CH_3CN solution at a scan rate of 50 mV s^{-1}.

and the edge are significantly blue-shifted compared to 380 nm for absorption maximum and 420 nm for absorption onset for poly(9,9-dialkyl-2,7-fluorene)s[13] and poly(9,9-dialkyl-2,7-silafluorene).[12] The optical band gap (Eg) of poly(9,9′-alkyl-3,6-silafluorene) was estimated at *ca.* 4.0 eV from the onset of the absorption edge (310 nm). Since poly(2,7-dialkyl-silafluorene)[12] shows a greater red-shifted absorption peak than that of poly(3,6-silafluorene), we tentatively attribute the observed remarkable blue shift of poly(3,6-silafluorene) to the reduction of conjugation of a polymer in 3,6-linkage in comparison with 2,7-linkage in silafluorene.

The PL spectrum of poly(3,6-silafluorene) was recorded at 290 nm excitation (Fig. 1). In solution, **VI** shows an emission maximum of 355 nm followed by two vibronic shoulders at 370 and 420 nm with a quantum efficiency of 30% in 1,2-dichloroethane solution (Table S1†). Unlike most other conjugated polymers, PL emission of polysilafluorene in the solid state shows almost no red shift in comparison with PL spectra in solution. This is consistent with the fact that the absorption spectra are identical in solution and the solid state. Similar results were obtained for **VII**, whose PL emission maximum was observed at 360 nm.

Fig. 2 shows the cyclic voltammograms of PSFC6C6 films cast on a platinum electrode. The onset of the irreversible oxidation wave of **VI** and **VII** is recorded at about +1.7 V, much higher than that of polyfluorene, +1.3 V.[13] The HOMO levels are estimated at −6.1 eV according to an empirical formula, $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}} + 4.4)$ (eV).[21] Unfortunately, we were unable to record the reduction potential of poly(3,6-silafluorene). The LUMO levels were estimated at around −2.1 eV from the HOMO level and the optical band gap of polysilafluorene.

In summary, soluble poly(9,9′-alkyl-3,6-silafluorene) homopolymers were prepared by nickel catalyzed coupling reaction. The UV-vis absorption spectra show that the energy gap of poly(9,9′-alkyl-3,6-silafluorene) is about 4.0 eV. The PL spectra show an emission maximum at around 355 nm both in solution and in the solid state. To the best of our knowledge, this is the first conjugated polymer with a band gap of 4.0 eV and with the ultraviolet emission peaked at 355 nm.

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