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# Novel vinyl ether functionalized fluorene polymers for active incorporation into common photoresist matrices

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ABSTRACT

A novel vinyl ether functionalized fluorene monomer was prepared to produce a series of fluorene-based polymers with different emitter units to cover emission in the visible spectrum whilst retaining the same main absorption profile. The vinyl ether functionality allows for active incorporation of the light emitting polymers into standard vinyl ether and glycidyl ether photoresist materials. This enables photopatterning of light emitting structures for application in UV down-conversion, waveguiding and for lasing media.

Fluorene-based polymers are one of the most important light emitting materials used for organic optoelectronic devices. They are, for example used as the electro-active layer in organic LEDs[1] or in solar cells.[2] Lately, photoluminescing materials integrated in a photoresist matrix have attracted attention for a variety of applications.[3] These composites offer photolithographic patterning of photoluminescent structures. Fluorene polymers incorporated in a vinyl ether photoresist matrix have also been self-aligned over an inorganic micro-LED array,[3d] emitting UV light for down-conversion into the visible spectrum, producing hybrid inorganic/organic LEDs for high intensity display applications. The light emitting polymer/photoresist composites also show promising characteristics for waveguides and lasing media, because of their solution-like high fluorescence yields. Due to the recognized incompatibilities[4] between the vast majority of functional organics such as light emitting molecules and the materials used in conventional photolithography, a novel class of crosslinkable vinyl ether functionalized fluorene polymers is presented here.

These polymers can be actively incorporated in the photoresist network upon photocuring, retaining their solution fluorescence characteristics. The vinyl ether functionalized fluorene polymers are miscible with vinyl ether phororesists as well as with most glycidyl ether photoresist materials that were immiscible with polyfluorenes previously (e.g., SU8 and CHDG).[5]

The integration of green, orange and red emitters into the fluorene-based polymer backbone allows for tunable emission colours whilst retaining the fluorene backbone absorption at ~370 nm. This makes the materials presented beneficial for application in photonic multicolour arrays with just one excitation wavelength.

In this Letter, we report for the first time on the high yield preparation of 2,7-dibromo-9,9-(diethanol divinyl ether)fluorene monomer (**VE1**), and the Suzuki polycondensation with 9,9-dihexyl-2,7-fluorenediboronic acid bis(pinacol) ester (**B1**) and 2,7-dibromo-9,9-(dihexyl)fluorene (**E1**), 4,7-dibromo-2,1,3-benzothiadiazole (**E2**), 1,4-diketo-2,5-dihexyl-3,6-bis(4-bromophenyl)pyrrolo-[3,4-*c*]pyrrole (**E3**) and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**E4**) for blue, green, orange and red emission.

Scheme 1 illustrates the two-phase reaction using tetra-*n*-butylammonium bromide as a phase transfer catalyst to functionalize 2,7-dibromofluorene with ethyl vinyl ether groups at the 9,9-position of fluorene. All the starting materials are available from major fine chemicals suppliers. 2,7-Dibromofluorene, 2.5 equiv of chloroethyl vinyl ether and the phase transfer catalyst were dissolved in toluene before 50% wt/wt aqueous NaOH solution was added and the mixture was then refluxed overnight. After work-up and removal of the solvent under vacuum, a yellow oil was received that crystallized readily on standing.

The crude product was recrystallized from ethanol and pure **VE1** monomer was obtained in 95% yield. The $^1$H NMR spectrum showed the absence of the methylene protons at the 9,9-position of the fluorene and the characteristic quadruplet at 6.1–6.2 ppm

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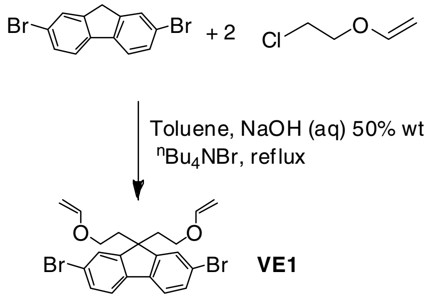


**Scheme 1.** The synthesis of 2,7-dibromo-9,9-(diethanol divinyl ether)fluorene monomer—the building block for the crosslinkable fluorene-based polymers.

due to the vinyl-methylidyne protons (for further information see supplementary data).

**E1** was purchased from Sigma–Aldrich. All other monomers were synthesized using literature procedures (**B1**,[6] **E2**,[7]**E3**,[8] **E4**[9]).

A standard Suzuki polycondensation using one equivalent of **VE1**, one equivalent of **E1–E4**, respectively, and 2 equiv of **B1** was applied as shown in Scheme 2. Tetrakis(triphenylphosphine)palladium(0) was used as catalyst and 2 M aqueous potassium carbonate solution as base. The mixture was reacted at a moderate temperature of 90 °C, to protect the vinyl ether functionalities from reacting, for two days to ensure full conversion.

The polymer was recovered after pouring the cooled organic phase into methanol. After filtration and drying at 40 °C in vacuo, the light emitting, crosslinkable polymers **P1–P4** were received in high to moderate molecular weights as shown in Table 1. The low molecular weight for **P4** and high polydispersity values may be a result of incomplete bromination of the emitter monomers and hence chain termination during polymerization may have occurred. Also, extraction methods to remove low molecular weight material were not used.

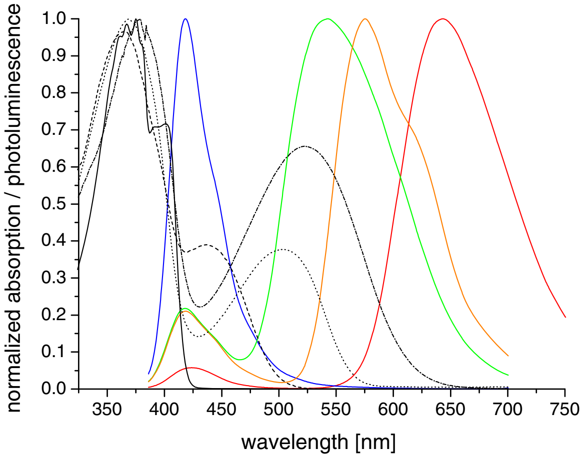
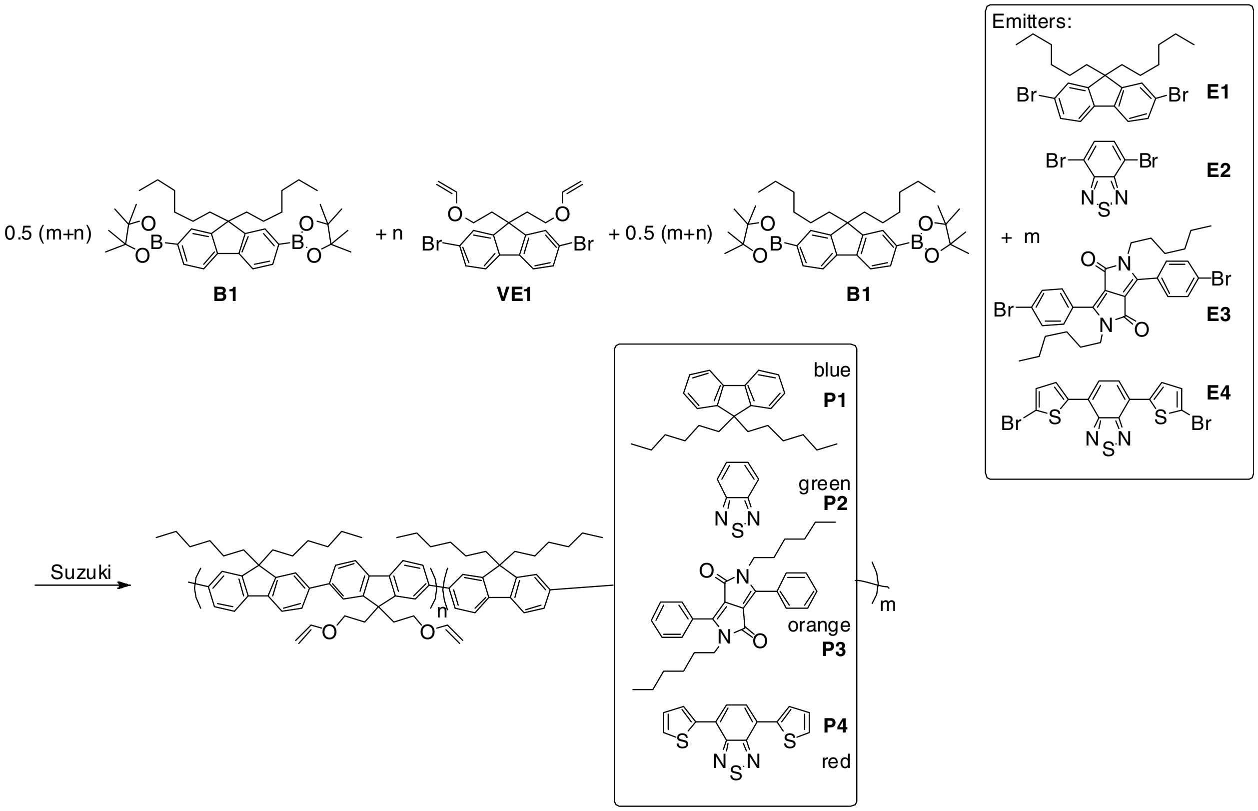


**Figure 1.** Normalized absorption and photoluminescence spectra of **P1–P4** showing their main absorption max at ~370 nm and photoluminescence in the blue, green, orange, red spectrum. Absorption spectra: **P1**: solid black, **P2**: dashed black, **P3**: dotted black, **P4**: dash-dotted black. Photoluminescence spectra: **P1**: blue, **P2**: green, **P3**: orange, **P4**: red.

UV absorption and fluorescence spectra were recorded from toluene solutions of **P1–P4**, as well as from photocured films of 0.1% wt/wt of the polymers in 1,4-cyclohexanoldivinyl ether (CHDV) with 1% wt/wt of photoacid (*p*-octyldiaryliodonium hexafluoroantimonate) as the photoresist system. The photoresist as the solvating matrix does not cause a solvatochromic shift on the fluorescing polymers compared to their toluene solutions.

All four polymers have an absorption maximum of ~370 nm as shown in Figure 1. However, **P2–P4** have a second much smaller maximum towards longer wavelength at 437 nm, 505 nm and 524 nm, respectively. These maxima are caused by the emitter



**Scheme 2.** The synthesis of polymers **P1–P4** bearing vinyl ether moieties for active incorporation in vinyl ether and glycidyl ether photoresist systems.

**Table 1**
Physical properties of polymers **P1**–**P4**

| Compound | $\lambda_{abs}$ [nm][a] | $\lambda_{PL}$ [nm] | $\phi_{toluene}$ ($\lambda_{ex}$ = 370 nm) | $M_w$[b] [g/mol] | $M_n/M_w^b$ |
|---|---|---|---|---|---|
| **P1** | 375 | 418 | 0.63 | 58500 | 3.2 |
| **P2** | 365, 437 | 545 | 0.45 | 122000 | 5.8 |
| **P3** | 370, 505 | 575 | 0.39 | 132000 | 6.2 |
| **P4** | 378, 524 | 645 | 0.31 | 8600 | 1.5 |

[a] Absorption maximum and second maximum from emitter unit absorption, where applicable.

[b] Determined by gel permeation chromatography (GPC), relative against polystyrene standards.

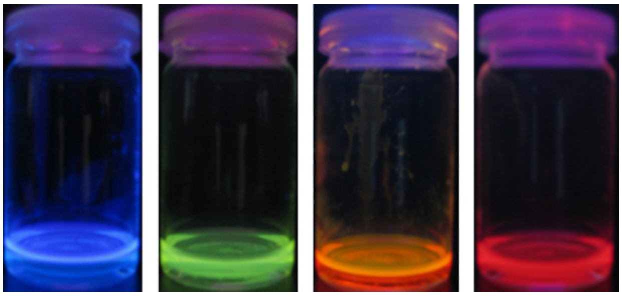


**Figure 2.** Photographs of **P1**–**P4** photocrosslinked in a CHDV matrix under 368 nm UV illumination.

units within the polymer backbone, which have a lower energetic band-gap. The photoluminescence spectrum of **P1** in the blue spectral range is comparable to that of ordinary poly-9,9-(dihexyl)fluorene, confirming that the vinyl ether moieties have no effect on the spectral performance of the fluorescing polymer. **P2**, **P3** and **P4** exhibit photoluminescence in the green, orange and red spectral ranges as can be seen in Table 1. **P2**–**P4** all show a negligible emission at ~370 nm that can be attributed to polyfluorene emission resulting from incomplete energy- transfer from the fluorene units into the emitter units.

Fluorescence quantum yields were determined in toluene by a comparative method, with anthracene as the standard. The excitation wavelength was held constant at 370 nm for all four polymers, since this is the absorption maximum associated with the fluorene segments in the backbone. **P1** has a quantum yield comparable to commercial polyfluorene. The quantum yields for **P2–P4** are somewhat lower than for **P1**. This is expected because during energy-transfer from the fluorene segments into the emitter units, energy can be lost via different mechanisms.[10]

When incorporated into a photoresist material, **P1**–**P4** are protected from environmental degradation, for example from oxygen or solvents.[3d,e] The light emitting polymers are solvated within the photoresist matrix and hence exhibit similar quantum yields as in toluene.

Figure 2 shows glass vials of photopolymerized films of 1% wt/wt of **P1**–**P4** in 1 g of CHDV with 1% wt/wt of photoacid generator under 368 nm UV illumination. The films were cured within 10 s of radiation from a 6 mW/cm$^2$, 368 nm broad area UV source. The short cure time can be attributed to the well-studied photoinduced electron transfer from the photon harvesting light emitting polymers to the photoacid generator.[10]

The environmental protection, short cure times and high fluorescence yield make the novel photocrosslinkable composites of CHDV and **P1**–**P4** attractive for direct laser writing applications and self-alignment over UV light sources. The resulting fluorescing structures have potential applications as waveguiding and lasing media.

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## Supplementary data

Synthetic procedures and $^1$H NMR spectra of **VE1** and **P1**–**P4** and more photographs of cured crosslinkable light emitting polymers and CHDV composites are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.05.133.

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