

Nearly pure blue photoluminescent poly{2,7-[9-{3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl}-9-(3,6-dioxaoctyl)]fluorene} in film[†]

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The first unsymmetrically substituted polyfluorene bearing a bulky poly(benzyl ether) dendron and less bulky 3,6-dioxaoctyl groups in the 9-position was designed and synthesized, which gives almost a pure bluish photoluminescence with negligible weak greenish excimer emission around 520 nm even in a thermally annealed thin solid film.

Recently, π -conjugated polyfluorene (PF) has been attracting intensive interest due to its bluish photo/electro-luminescence properties with high quantum yield.¹ However, greenish excimer emission and significant fluorescence quenching generally occur for this blue light emitter in a solid film.² Among the methods to avoid the detrimental π -aggregation behavior,³ much effort has been made to introduce bulky dendrons like poly(benzyl ether) (Fréchet-type) or polyphenylene into the conjugated polymer backbone, *i.e.*, end-capping of poly[2,7-(9,9-di-*n*-hexyl)fluorene]⁴ and symmetrically 9,9-bis-substituted PFs.⁵ The resulting PFs have been found to significantly suppress the excimer emission even in their thermally annealed solid films. In addition to these symmetrically 9,9-bis-substituted PFs, the unsymmetrically substituted PF having two different side groups in the 9-position has also attracted much attention.⁶ As an example, a PF bearing two different methyl and 4-cyanobutyl groups in the 9-position was designed and synthesized towards water-soluble conjugated polymer.^{6b} Based on the assumption that a regio-random PF bearing two different substituents in the 9-position may significantly suppress the π -aggregation in a solid film to decrease the greenish excimer emission and the combination of bulky dendrons with less bulky groups will increase the luminophore density, thereby producing a strong luminescence, we have designed and synthesized a new unsymmetrically substituted PF **4** (Scheme 1) bearing semiflexible bulky poly(benzyl ether) dendrons and linear 3,6-dioxaoctyl groups in the 9-position. We now report that **4** emits almost a pure blue color photoluminescence even in a thermally annealed thin solid film, while the greenish excimer emission was drastically suppressed even compared to the corresponding 9,9-bis-dendron-substituted **5**.

The synthetic procedures are outlined in Scheme 1. The resulting 2,7-dibromo-9-lithiofluorene from 2,7-dibromofluorene (**1**) (Aldrich) and 2-fold lithium diisopropylamide (LDA) (Aldrich) was reacted with an equivalent amount of 1-bromo-3,6-dioxaoctane (Lancaster) at -60 to 25 °C in THF, yielding 2,7-dibromo-9-(3,6-dioxaoctyl)fluorene (**2**).⁷ Using the phase transfer catalyst, triethylbenzyl ammonium chloride (Kanto), the monomer **3** was synthesized from **2** and 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl bromide (**R-Br**) (TCI). The conversion was almost quantitative, which was evidenced by the complete disappearance of the triplet signal of 9-H at 4.10

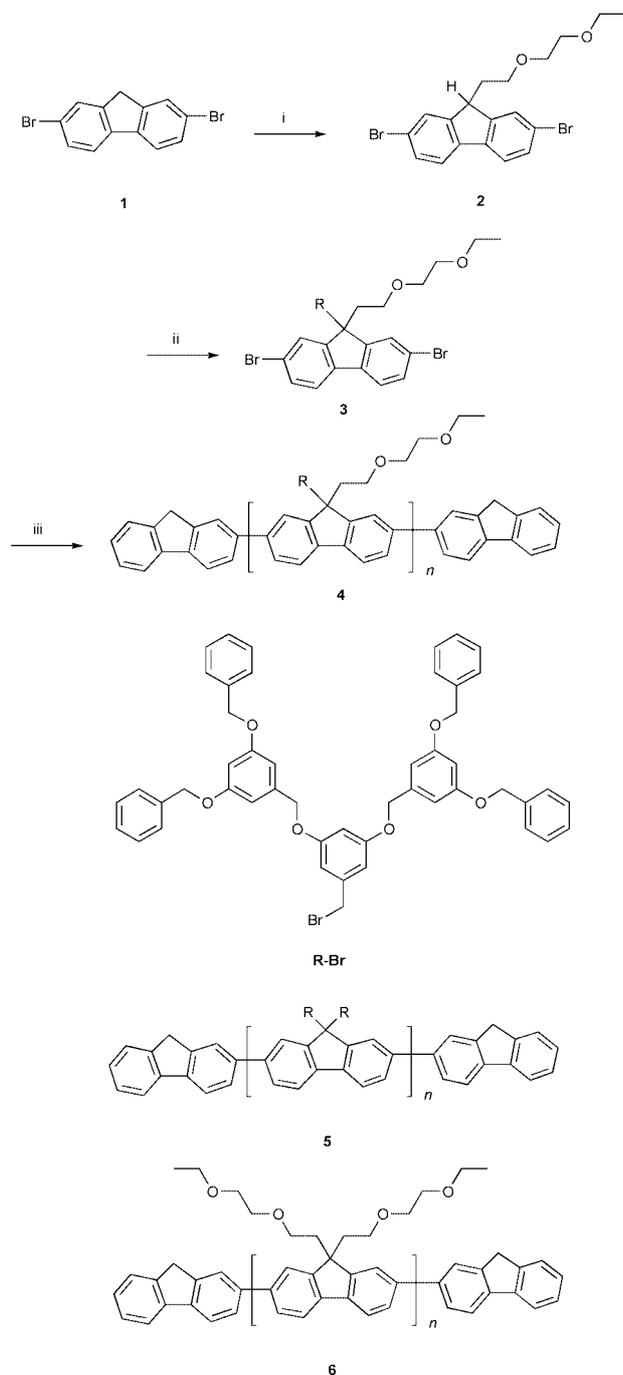
ppm in the ¹H NMR spectrum. Polymerization was carried out using the zero-valent nickel reagent, bis(1,5-cyclooctadiene)-nickel(0) (Ni(COD)₂) (Kanto), and the end-termination was accomplished using 2-bromofluorene (Acros).⁸ For a comparison of the photophysical properties with **4**, the two corresponding symmetrically 9,9-bis-substituted **5** and **6** were also synthesized using previously reported method.⁸ The structures of all the synthesized monomers and PFs were confirmed by NMR and elemental analysis.[†]

PF **4** as well as **5** is highly soluble in common organic solvents, *e.g.*, THF, toluene and chloroform, but **6** has limited solubility in THF and toluene although it is readily soluble in chloroform. The molecular weights of **4**, **5** and **6** (soluble part in THF) estimated by gel permeation chromatography (GPC) versus the polystyrene standards in THF at 30 °C are $M_w = 26,300$ (M_w/M_n , 2.0), $M_w = 32,700$ (M_w/M_n , 1.7), and $M_w = 381,300$ (M_w/M_n , 2.6), respectively. Differential scanning calorimetry (DSC) (heating at 10 °C min⁻¹ at the second run) revealed that **4** and **5** have softening points at around 58 °C and 62 °C, respectively, evidenced by the endothermic peaks, while **6** exhibits a melting point of 182 °C.

As shown in Fig. 1, the UV-vis spectrum of **4** in THF solution exhibits two absorption bands at 386.0 nm ($\epsilon = 3.1 \times 10^4$ (fluorene-repeating-unit)⁻¹ dm³ cm⁻¹) and 284.0 nm ($\epsilon = 1.1 \times 10^4$ (fluorene-repeating-unit)⁻¹ dm³ cm⁻¹), probably ascribed to the π - π^* transition of the conjugated polymer backbone and the phenylene in the side dendrons, respectively. The $\lambda_{\max, \text{abs}}$ of **4** exhibits only a slight red shift of 2 nm compared to that of **5** ($\lambda_{\max, \text{abs}}$, 384.0 nm), implying that the number of bulky dendron side chains does not affect the torsion angle in the conjugated polymer backbone, but shows a large blue shift of 8.5 nm compared to that of **6** ($\lambda_{\max, \text{abs}}$, 394.5 nm), probably due to the larger steric hindrance impacted by the bulky dendrons than the two less bulky 3,6-dioxaoctyl groups. The photoluminescence (PL) spectrum of **4** in THF solution exhibits the two characteristic sharp peaks at 415.0 and 437.0 nm and a low energy shoulder near 470.0 nm, almost identical to those of the corresponding **5** ($\lambda_{\max, \text{emi}}$, 414.0 nm, excited at 384.0 nm) and **6** ($\lambda_{\max, \text{emi}}$, 417.0 nm, excited at 394.5 nm). The quantum yield of **4** in THF is estimated to be 58%, comparable to 54% of **5** and 53% of **6**.[†]

Fig. 2 compares the UV-vis and PL spectra of **4-6** in the thermally annealed thin solid films. The UV-vis spectrum of **4** in the film exhibits no absorption band broadening except for the $\lambda_{\max, \text{abs}}$ showing a minute red shift of 2.5 nm in comparison to that in THF solution. This is similar to **5** in the film and THF solution. On the other hand, **6** in the solid film gave a UV-vis spectrum with a significantly broadened absorption band and a new absorption peak around 399 nm compared to that in THF solution, indicating that a specific intensive aggregation formed. The PL spectrum of **4** in the film shows two characteristic $\lambda_{\max, \text{emi}}$ s at 423.0 and 447.5 nm and a tail in the range 500 to 700 nm. On the other hand, **5** gave a PL spectrum with a featureless long wavelength emission (excimer emission)

[†] Electronic supplementary information (ESI) available: characterization data for **2**, **3**, and **4**, and measurement details of the quantum yield in THF solution. See <http://www.rsc.org/suppdata/cc/b1/b108097k/>



Scheme 1 Reagents and conditions: i, 2-equimolar LDA, THF, 1-bromo-3,6-dioxaoctane, -60 to 25 °C, 3 h, 60%; ii, **R-Br**, 50% aq. NaOH, DMSO, triethylbenzyl ammonium chloride, 25 °C, overnight, $\sim 100\%$; iii, $\text{Ni}(\text{COD})_2$ -1,1'-bipyridyl (1 : 1, mol/mol), COD, DMF-toluene (1 : 4, v/v), 80 °C, 4 d; 2-bromofluorene in toluene, 4 h, 80%.

band around 520 nm, which is much weaker than that for **6**, indicating that the steric impact of the dendritic substituents significantly suppresses the intermolecular π -stacking of the polymer backbone. The weak excimer emission for **5** could be due to the liquid crystalline property already reported for the poly(phenylenevinylene)s having poly(benzyl ether) dendron side chains.⁹ The almost negligible weak excimer emission for **4** in the film might result from an amorphous structure caused by the regio-random backbone structure, which is possibly related to the lower softening point than that of **5**. Thus, the replacement of one dendron with a less bulky substituent in the 9-position enables almost pure blue photoluminescence.

In conclusion, the first well-defined unsymmetrical-substituted **4** bearing bulky poly(benzyl ether) dendron and less bulky 3,6-dioxaoctyl substituents in the 9-position gave almost a pure

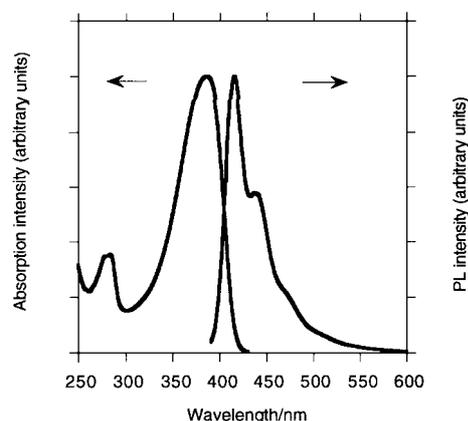


Fig. 1 UV-vis absorption (3.0×10^{-5} mol L^{-1} of the fluorene-repeating-unit) and PL (1.4×10^{-6} mol L^{-1} of the fluorene-repeating-unit) spectra of **4** (excited at 386.0 nm) in THF solution at 25 °C.

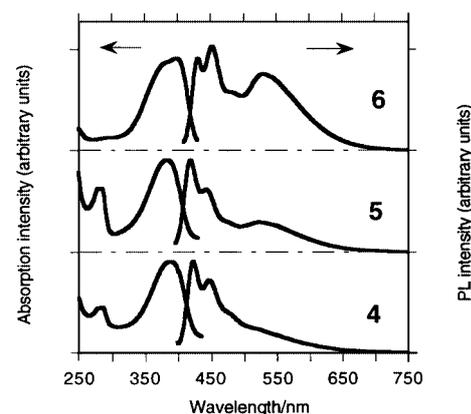


Fig. 2 Normalized UV-vis absorption and PL spectra of **4** (excited at 388.5 nm), **5** (excited at 384.5 nm) and **6** (excited at 399.0 nm) in thin solid films prepared by the spin-coating method from chloroform solution ($\sim 10^{-2}$ mol L^{-1} of the fluorene-repeating-unit) on a quartz substrate upon annealing at 200 °C for 3 h *in vacuo* followed by slow cooling to 25 °C.

bluish photoluminescence with negligible weak greenish excimer emission around 520 nm even in the thermally annealed thin solid film, showing the great potential for the construction of large-area blue light emitters.

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