# Blue Light Emitting Poly(*N*-arylcarbazol-2,7-ylene)s

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*N*-(4-alkoxyphenyl) substituted poly(carbazol-2,7-ylene)s were synthesized by Ni-catalyzed polycondensations of 2,7-dihalogenocarbazoles. The polymers intensely fluoresced blue in solution and in the solid-film state by irradiation of UV light. The introduction of the aryl group at the *N*-position of poly(carbazol-2,7-ylene) enhanced fluorescent quantum efficiency of the polymer, which showed higher performance than *N*-alkyl substituted polymers.

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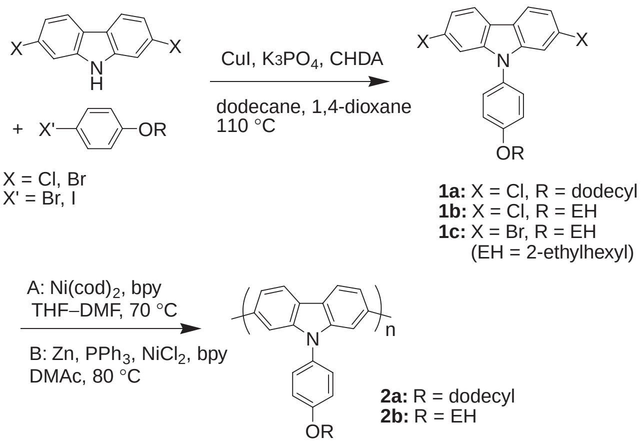
Development of blue light emitting polymers with high performance such as good stability, pure blue color emitting, and high quantum efficiency is inevitable to be applied in light emitting diodes (PLED) for full color displays.[1] Conjugated polymers have a merit to efficiently emit even in the solid thin-film state, which can simplify the process for fabrication of organic LEDs by an appropriate manner such as spin coating and ink-jet printing. Recently, poly(*N*-alkylcarbazol-2,7-ylene)s have been considered as a candidate for blue light emitters instead of fluorene-based polymers.[2] Poly(carbazol-2,7-ylene) is regarded as a poly(4,4′-biphenylylene) consisting of the strained planner unit of imino-bridged biphenylylene, which must show a similar properties to polyfluorene.[3] Furthermore, a remarkable feature of pyrrole-based conjugated polymers is a relatively high HOMO level around $-5.5$ eV,[3,4] which might be more advantageous than polyfluorene for hole injection from the indium tin oxide (ITO) anode in the PLED device. In this paper, we investigate potential of poly(carbazol-2,7-ylene)s as the blue light emitter by modifying the polymer appropriately.

In our previous investigations of the pyrrole-based polymers,[4] photoluminescent (PL) property of polypyrroles could be largely improved from almost non-emissive to good luminescent by introducing aromatic moieties in the emissive core unit, which suggested that increase of rigidity and extended $\pi$-conjugation at the emissive core enhanced the PL efficiency. By contrast, the increase of rigidity on the conjugated polymer backbone decreased solubility of the polymer in organic solvent. In addition, excimeric PL emission sometimes seriously influences the efficiency and purity of the emitting color. Considering the above mentioned, phenyl groups with long alkoxy side chains are introduced into the *N*-position of poly(carbazol-2,7-ylene).

The synthetic route of poly(*N*-arylcarbazol-2,7-ylene)s is summarized in Scheme 1. N-Arylation of 2,7-dichlorocarbazole[2] with 1 equiv. *p*-alkoxybromobenzene was carried out by the CuI-*trans*-1,2-cyclohexanediamine (CHDA)-catalyzed method,[5] affording monomers in good yields (**1a**: 95%, **1b**: 89%), respectively. In the case of N-arylation of 2,7-dibromocarbazole,[6] 5 equiv. *p*-alkoxyiodobenzene was reacted under the same conditions (**1c**: 50%). The monomers were polymerized by Yamamoto coupling reactions either with 2.4 equiv. Ni(cod)$_2$ and 2.4 equiv. 2,2′-bipyridine (bpy) in THF–DMF at 70 °C for 1.5 days (method A) or with 2.5 equiv. Zn, 0.6 equiv. PPh$_3$, 0.05 equiv. bpy, and 0.05 equiv. NiCl$_2$ in *N*,*N*-dimethylacetamide at 80 °C for 3 days (method B).[2] The results of the polymerizations of monomers **1** are summarized in Table 1.



**Scheme 1.** Synthesis of poly(*N*-arylcarbazol-2,7-ylene)s **2**.

**Table 1.** Polymerization results of **1**

| Monomer (Method) | Polymer | Yield /% | $M_n$[a] | $M_w/M_n$ | d.p.[b] |
|---|---|---|---|---|---|
| **1a** (A) | **2a** | 68 | 6000 | 1.5 | 14 |
| **1b** (A) | **2b** | 77 | 6600 | 1.2 | 18 |
| **1b** (B) | **2b** | 89 | 7700 | 1.9 | 21 |
| **1c** (B) | **2b** | 75 | 4700 | 1.4 | 13 |

[a]The number-average and the weight-average molecular weights ($M_n$ and $M_w$) were determined by gel permeation chromatography vs polystyrene standards (THF). [b]The degree of polymerization was estimated from $M_n$.

In all cases, polymers **2** were obtained as a pale-yellow powdery solid in good yields, respectively. The polymers **2** obtained after purification by reprecipitations were soluble in usual organic solvents such as THF and CHCl$_3$. They showed a good thermal stability with a high glass transition temperature ($T_g > 150$ °C) and a high softening temperature ($T_s > 210$ °C). The chemical structure of **2** was confirmed by NMR.[7] All polymers have a good processability to make a thin cast film.

The polymers **2** showed an intense blue fluorescence in solution and in the solid thin-film state. Optical properties of **2** are summarized in Table 2, and the typical spectra of absorption and PL both in solution and in the thin solid-film state are shown in Figure 1.

The polymers **2** showed a UV–vis absorption band due to $\pi$–$\pi^*$ transition around 300–400 nm. In the case of **2a** having the long dodecyl side chain, the absorption spectrum broadened in the solid state, and there was a considerable difference of absorption maximum ($\lambda_{max}$) in CHCl$_3$ solution and in the solid state. The difference might be attributed to interchain interactions.

**Table 2.** Optical properties of the polymers **2**

| Polymer (method) | Solution $\lambda_{\max}$ (nm) abs. | Solution $\lambda_{\max}$ (nm) Em[c] | Thin solid $\lambda_{\max}$ (nm) abs. | Thin solid $\lambda_{\max}$ (nm) em. | $\phi_f$[d] |
|---|---|---|---|---|---|
| **2a** (A)[a] | 380 | 418 | 418 | (441) 467 | 0.87 |
| **2b** (A)[a] | 379 | 420 | 381 | 432 | $\approx 1$ |
| **2b** (B)[a] | 384 | 417 | 389 | 433 | $\approx 1$ |
| **2b** (B)[b] | 372 | 415 | 373 | 428 | 0.80 |

[a] Prepared from 2,7-dichlorocarbazole monomers (**1a** and **1b**). [b] Prepared from 2,7-dibromocarbazole **1c**. [c] The polymer concentration was about $10^{-6}$ mol/dm$^3$. [d] Fluorescence quantum yields ($\phi_f$) were determined in $CHCl_3$ against 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.9$) as the standard.

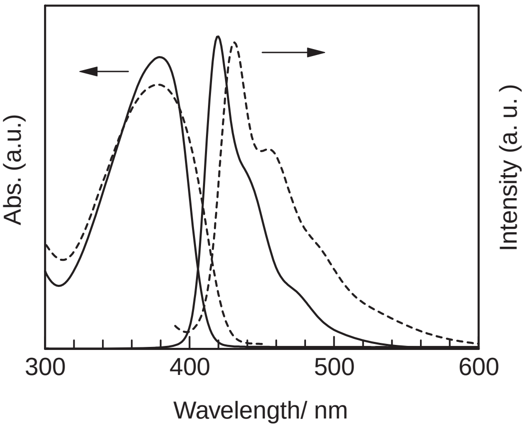


**Figure 1.** UV–vis absorption and fluorescence spectra of **2b** in $CHCl_3$ (solid line) and in the solid state (broken line).

By contrast, **2b** having the branched 2-ethylhexyl (EH) side chain showed the absorption $\lambda_{\max}$, both in the solution and in the solid state, was around 380 nm (Figure 1). This suggests that **2b** has very similar conformations in both states. From the absorption edge observed in the thin-film samples, HOMO–LUMO energy gap ($E_g$) is estimated to be 2.80 eV for **2a** and 2.90 eV for **2b**, respectively. The HOMO level is also determined by electrochemical method,[8] being about $-5.8$ eV.

PL spectra of **2b**, which was symmetrical with a vibronic fine structure to the absorption spectra, showed a maximum emission ($\lambda_{\max}$) around 420 nm in $CHCl_3$ and 430 nm in the solid state (Figure 1). Almost the same and narrow shape of the emission spectra with slight difference of fluorescence $\lambda_{\max}$ suggests that the emission is essentially the same both in solution and in the solid state without formation of excimer. The degree of polymerization and the terminal residue influence the optical properties. On the other hand, **2a** showed wider spectrum than **2b** in the solid state, and the emission $\lambda_{\max}$ shifted longer in wavelength (Table 1). The symmetrical Gaussian fitting of the fluorescence spectrum for **2a** suggests that the spectrum is composed of three peaks at 434, 461, 493 (shoulder) nm. The peak around 430 nm may be formed by the radiative singlet exciton decay with the Stokes' shift of 50 nm and the most intense peak around 465 nm may be attributed to the radiative decay of excimer. The Stokes' shifts are small within about 40 nm in solution and 50 nm in the solid state. The fluorescence quantum efficiency of **2** in $CHCl_3$ is almost quantitative.

In conclusions, increase of rigidity at the absorption and emitting core in poly(carbazol-2,7-ylene) by introducing the aryl group enhanced quantum efficiency in comparison with poly(*N*-alkylcarbazol-2,7-ylene)s ($\phi \approx 0.8$).[2] The branched 2-ethylhexyl side chain effectively worked disturbing formation of excimers. The polymerization of **1** by Zn with the Ni catalyst (method B) was enough to obtain the polymer with good optical properties, which had a merit without using the hazardous Ni(cod)$_2$. Furthermore, preliminary manufacturing of PLED device with **2** (method A) composing of ITO/PEDOT(PSS)/**2**/Ca–Al realized the blue emission the same to the PL spectra in the solid state at a low turn on voltage ($\approx$3 V) with a maximum luminance (about 2000 cd/m$^2$) and an efficiency ($\eta_c$) $> 0.2$ cd/A at 10 V, which was superior to those of poly(*N*-alkylcarbazol-2,7-ylene)s. The bridged triphenylamine structure might affect a hole transporting ability of **2**, which resulted in an appropriate bipolar valance of the device.

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