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CHEMISTRY

Novel Bipolar Carbazole-Containing Polyphenylquinoxalines: Synthesis and Photophysical Properties

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In recent time, conjugated electroluminescent polymers have attracted much attention from both the scientific and practical viewpoint due to their application as electroactive materials for light-emitting diodes [1–3]. It has been found that intense electroluminescence (EL) in polymer requires high electron–hole conduction of a medium related to the mobility of charge carriers and a balance of injection of carriers of both signs from opposite electrodes into the emission polymeric layer. However, the majority of EL polymers are hole-transport materials, which leads to the imbalance of charge injection and a poor quantum yield. A search for new efficient electron-transport polymers is required to improve performance of electrooptical devices, which is achieved in particular by introducing into macromolecules electron-withdrawing fragments: triazole [4], oxadiazole [5], quinoline [6], and quinoxaline [7]. The latter is the least studied. One can suppose that polyphenylquinoxalines (PPQs) will show higher electron-withdrawing properties owing to the presence of four electron-withdrawing heteroatoms. A promising approach to improve the quantum yield is provided not only by the balance of the electron and hole conduction but also by design of multilayer bipolar (donor–acceptor) emission polymers.

In this work, to solve this problem, we have used a combination of carbazole- and quinoxaline-containing fragments in PPQ macromolecules. Such molecules are known to show high thermal and oxidative stability, good mechanical and film-forming properties, and solubility in organic solvents [8]. In continuation of our studies [9–11], we have prepared and studied novel bipolar carbazole-containing PPQs as efficient electron–hole and transport materials; for this purpose, we obtained previously unknown bis(α-diketone) **III**. A common method for the synthesis of bis(α-diketone)s is the oxidation of bis(phenylethynyl)arenes obtainable from aromatic dibromides and arylacetylene.

We have proposed a new method for the synthesis of bis(α-diketone) **III** by the nucleophilic substitution reaction of fluorodiketone **II**, already containing bis(α-dicarbonyl) groups, with dicarbazole **I** according to Scheme 1.

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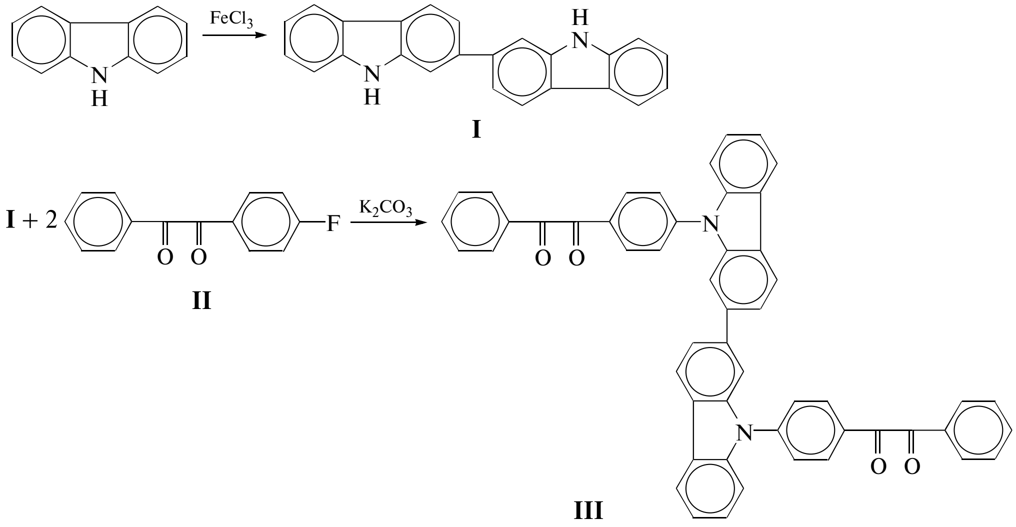
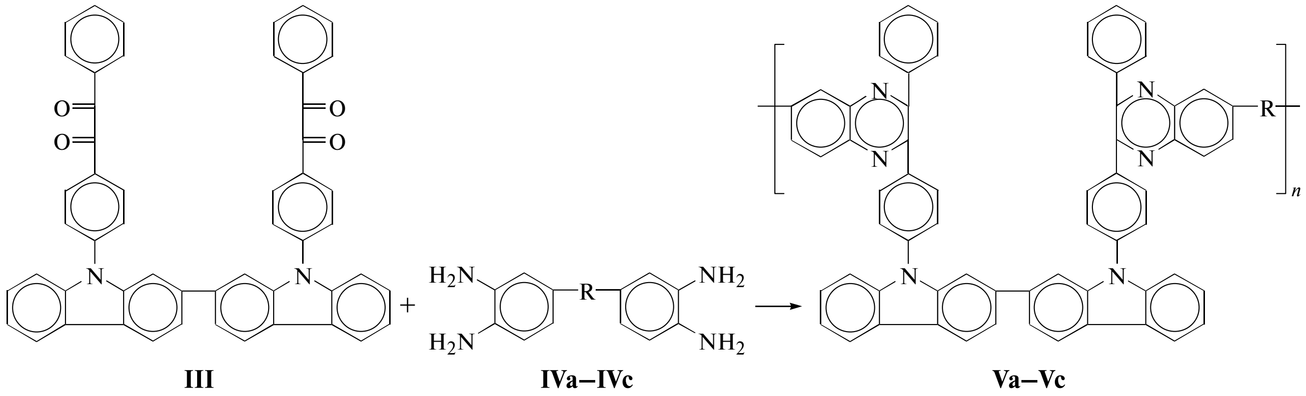


Scheme 1.

The reaction led to compound **III** in good yield (88%) without affecting the carbonyl groups. The composition and structure of target compound **III** were confirmed by elemental analysis data, IR spectroscopy, and ^{1}H and ^{13}C NMR. In particular, the IR spectra of the bis(α-diketone) show strong absorption bands in the region of 1665 cm^{-1} typical for the C=O group of α-diketone fragment.

The ^{1}H NMR spectra of compound **III** show three multiplets at δ = 8.1–8.3 (4H), 7.7–7.8 (6H), and 7.4–7.58 (4H) ppm, one singlet at δ = 8.37 ppm, one doublet at 7.99 ppm (4H, J = 8.1 Hz), and three well resolved triplets at δ = 7.64 (2H), 7.4 (2H), and 7.32 (2H, J = 7.2 Hz) ppm. Signal assignment in these spectra was made on the basis of integrated intensity ratio and spin–spin coupling constants (Fig. 1a). The ^{13}C NMR spectra of compound **III** in the range of δ = 110–150 ppm show 20 intense signals, eight of which are due to quaternary carbon atoms. A feature of these spectra of compound **III** is the presence of downfield signals of two different carbonyl groups of the α-diketone fragment at δ = 194 and 193 ppm (Fig. 1b).

Bis(α-diketone) **III** was used for the synthesis of PPQs containing dicarbazole groups in the main chain of macromolecules according to Scheme 2.



(R = – (a), $-CH_2-$ (b), –O– (c)).

Scheme 2.

Polymers **Va**–**Vc** were obtained by the reaction of aromatic tetraamines **IVa**–**IVc** with bis(α-diketone) **III** in an *m*-cresol solution at 190°C for 7 h. The reaction proceeded homogeneously to give the polymers with high viscosity characteristics (η = 0.79–0.94 dL/g). The structure of the polymers was confirmed by the data of IR and NMR spectroscopy. The IR spectra of the prepared polymers lack absorption

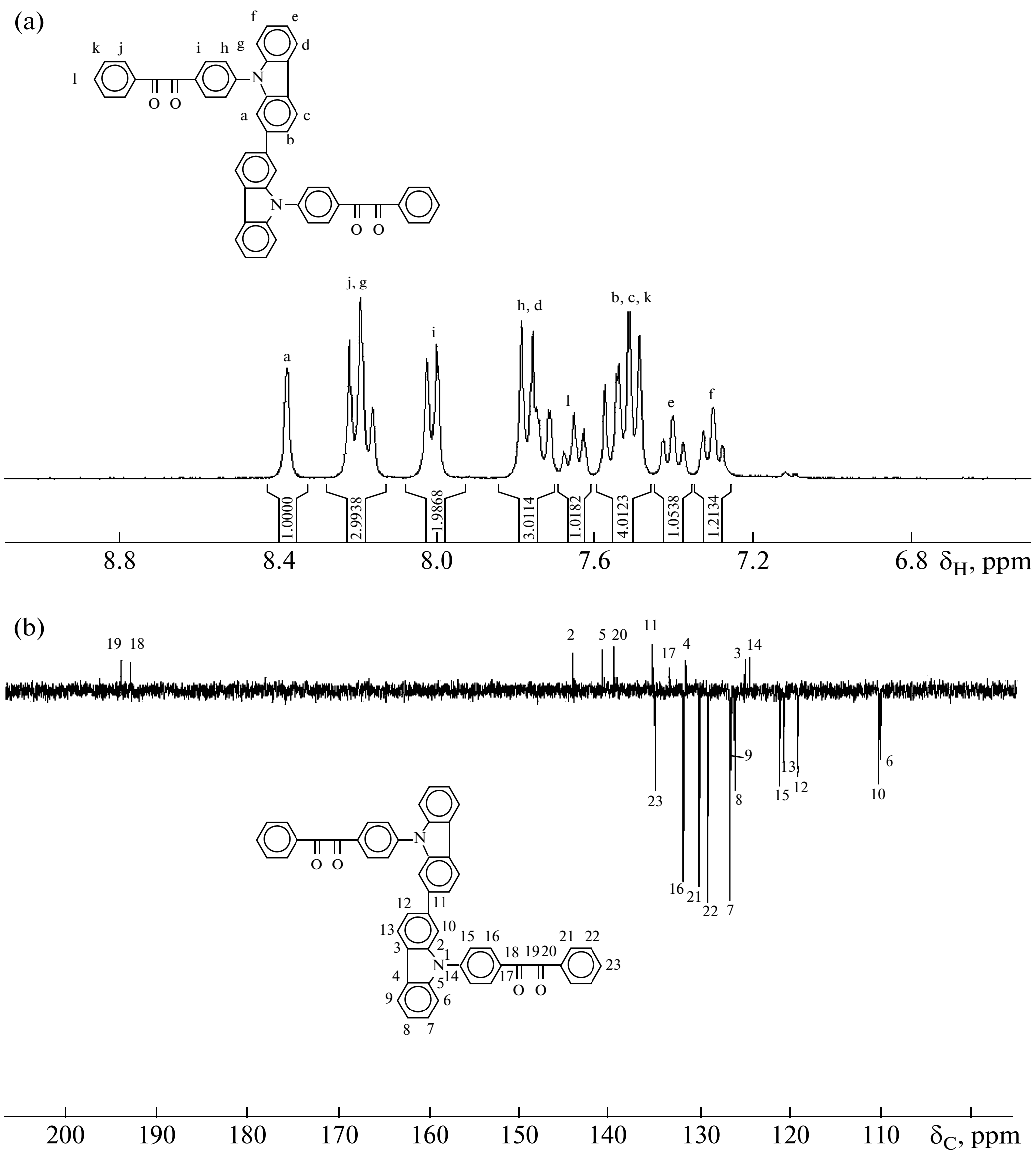


Fig. 1. (a) ^{1}H and (b) ^{13}C NMR spectra of compound **III**.

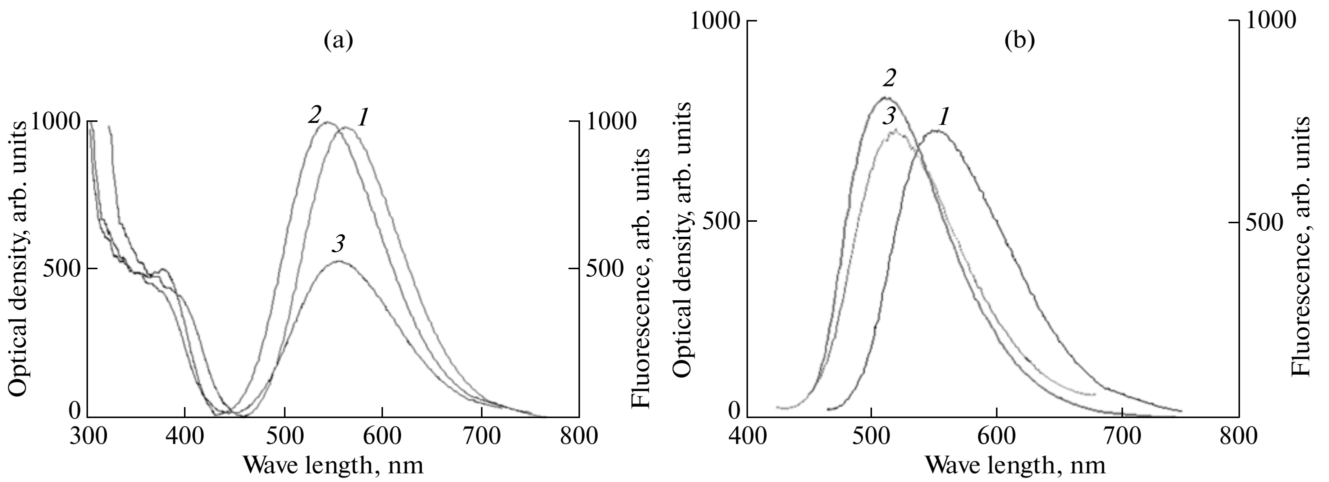


Fig. 2. Fluorescence spectra of polymers (*1*) **Va**, (*2*) **Vb**, and (*3*) **Vc** in (a) chloroform ($c = 10^{-4}$ mol/L) and (b) films.

Table 1. Certain characteristics of PPQs

Polymer	R	η_{red} (25°C, DMF), dL/g	T_g, °C	$T_{10\%}$, °C		Tensile properties of films	
				argon	air	σ, MPa	ε, %
Va	–	0.92	340	630	610	127	46
Vb	$-CH_2-$	0.81	315	610	590	95	52
Vc	–O–	0.75	329	615	600	100	62

Table 2. Certain photophysical characteristics of polymers **V** in solution and as films

Polymer	$\lambda_{abs, max}$, nm*		E_{opt}, eV**	λ_{beg}, nm***	$\lambda_{fl, max}$, nm****	
	solution	film			solution	film
Va	430	426	2.51	493	564	554
Vb	410	408	2.64	469	544	510
Vc	420	416	2.61	476	554	520

* Absorption spectra maximum of polymers.
** Optical gap width of a polymer determined from the equation $E_{opt} = 1240/\lambda_{beg}$.
*** λ of the beginning of absorption spectra in films.
**** Maximum of the fluorescence spectra of polymers.

bands in the ranges of 3200–3400 and 1660–1680 cm^{-1} related to the stretching vibrations of the C=O and NH_2 groups of the initial compounds, and show absorption bands at 1640 cm^{-1} typical of the C=N bonds in quinoxaline rings. The ^{13}C NMR spectra of all the polymers also lack signals at $\delta = 190–195$ ppm due to α-diketone fragments. The thermal properties of the polymers were studied by DSC and TGA within 250–700°C range. Some of PPQ characteristics are given in Table 1. Glass transition temperatures found from DSC curves are within 315–340°C. According to TGA in air and argon, all PPQs begin to lose 10% of weight at 590–610 and 610–630°C, respectively, depending on chemical structure. Good solubility of PPQs in organic solvents (*m*-cresol, NMP, phenols) allowed preparation from solution polymer films showing tensile strength $\sigma = 95–127$ MPa and specific elongation $\varepsilon = 46–62\%$ (Table 1).

The photophysical properties of polymers **Va**–**Vc** were studied by UV and photoluminescence spectroscopy in solution or as thin films (some their characteristics are shown in Table 2). The absorption maxima for chloroform solutions and thin films are within 410–430 and 408–426 nm, respectively. PPQs exhibit strong fluorescence in chloroform. All the compounds show green emission with fluorescence maxima in the range of 544–564 nm. The polymers as solid films also fluoresce with maxima within 510–554 nm. Polymer **Va** shows a bathochromic shift as compared with other compounds probably on account of the conjugation chain extension. The optical gap widths (E_{opt}) determined from the absorption spectra of films are in the range 2.51–2.64 eV. Typical fluorescence curves in solution and solid films are shown in Fig. 2.

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