



# Specific spectral characteristics of some phenylquinoxaline derivatives



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## ABSTRACT

Absorption and emission spectral characteristics of a bis(hydroxyphenylquinoxaline) Q, and two aromatic polyethers containing phenylquinoxaline rings, Q-DBF and Ox-Q, were studied in various solvents. Q, Q-DBF and Ox-Q display two absorption bands, while a poly(1,3,4-oxadiazole-ether) Ox-BisA, exhibits a single absorption band. Their fluorescence spectra ( $2.5 \times 10^{-6} \text{ mol L}^{-1}$ ) were characterized by an emission band between 380 and 520 nm. At slightly lower concentrations ( $6.4 \times 10^{-7} \text{ mol L}^{-1}$ ) and under excitation with light corresponding to the highest energy absorption band, Q-DBF and Ox-Q in ethyl acetate and cyclohexane solutions exhibited simultaneously dual emission bands in the near-UV ( $\approx 355 \text{ nm}$ ) and blue region ( $\approx 432 \text{ nm}$ ). The emission characteristics were quantified by CIE indices (in x, y color coordinates) for the investigated systems. Values of fluorescence quantum yields ranging from 15.93 to 49.83% in chloroform media were obtained.

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## 1. Introduction

Poly(aryl-ether)s represent a class of polymers well known as engineering thermoplastics with desirable properties, such as melt and solution processability, chemical stability and high glass transition temperature. The aromatic part of these polymers contributes to thermal stability and good mechanical properties, and the ether linkages facilitate the polymer processing while maintaining oxidative and thermal stability [1]. The introduction of heterocyclic units, such as phenylquinoxaline or 1,3,4-oxadiazole rings, into the main chains of aromatic poly(aryl-ether)s leads to polymers with good solubility, increased glass transition temperature and high thermal stability [2,3]. Aromatic poly(aryl-ether)s containing these heterocyclic units show improved solution and melt processing characteristics as compared to their counterparts containing only aromatic rings. These polymers can be prepared by nucleophilic displacement to form ether linkages during the polymerization reaction. For example, poly(aryl-ether phenylquinoxaline)s can be prepared by polymerization of bisphenols with bis(fluorophenylquinoxalines) [3], by reacting self-polymerizable phenylquinoxaline monomers [4,5], or by the reaction of bisphenols containing phenylquinoxaline rings with aromatic electrophiles such as 4,4'-difluorobenzophenone or 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole [6].

Aromatic poly(oxadiazole ether)s are of special interest due to their various physico-chemical properties and their potential use as electron-transporting materials or electroluminescence materials in organic light emitting diodes. Due to their optoelectronic properties, high thermal

stability and good mechanical properties, poly(oxadiazole ether)s play an important role in materials science [7–9].

Generally, dual fluorescence of different compounds is of great significance in their application in multifunctional sensor microarrays and other microscale sensor systems [10]. The dual fluorescence of many chromophores can be attributed to different processes occurring in the system, such as tautomerism [11], formation of two different excited states [12–15], conformational changes, excimer/excimer formation [16], excited-state intramolecular proton transfer (ESIPT) [17], and twisted intramolecular charge transfer (TICT) [18].

The present work focuses on the characterization of a series of phenylquinoxaline derivatives, one of them containing 1,3,4-oxadiazole rings, by using optical absorption, fluorescence, emission quantum yields and emission lifetime measurements. The photophysical properties of the phenylquinoxaline derivatives have been investigated in dilute solutions of various solvents (cyclohexane, toluene, chloroform and ethyl acetate) and in solid state. Their emission properties in chloroform were compared using a chromaticity diagram.

## 2. Experimental

### 2.1. Materials

Bis(hydroxyphenylquinoxaline), Q, was synthesized by the reaction of 4-hydroxybenzil with an aromatic tetraamine, 3,3'-diaminobenzidine, according to a previously published method [19]. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole was prepared from 4-fluorobenzoic acid and hydrazine hydrate, in polyphosphoric acid, according to the literature [20].

Poly(phenylquinoxaline ether ketone), Q-DBF, and poly(phenylquinoxaline-1,3,4-oxadiazole ether), Ox-Q, were synthesized by the

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conventional aromatic nucleophilic substitution polymerization technique of bis(hydroxyphenylquinoxaline) with 4,4'-difluorodiphenyl ketone or with 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, respectively. Poly(1,3,4-oxadiazole ether), Ox-BisA was prepared by the same synthetic procedure from 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and 2,2-bis(4-hydroxyphenyl)propane [21].

Q-DBF Yield: 90%. FTIR (film,  $\text{cm}^{-1}$ ): 3060 (C–H aromatic), 1653 (C = O), 1592 (C–C aromatic), 1344 and 1310 (phenylquinoxaline ring), 1236 (aromatic ether group).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.60 (2H, s), 8.31 (2H, d), 8.26 (2H, d), 7.81 (4H, d), 7.55 (8H, m), 7.37 (6H, d), 7.05 (8H, m).

Ox-Q Yield: 92%; FTIR (film,  $\text{cm}^{-1}$ ): 3057 (C–H aromatic), 1598 (C–C aromatic), 1342 (phenylquinoxaline ring), 1241 (aromatic ether group), 1012 and 977 (oxadiazole ring).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.61 (2H, s), 8.32 (2H, d), 8.25 (2H, d), 8.11 (4H, d), 7.61 (8H, d), 7.42 (6H, s), 7.16 (4H, d), 7.07 (4H, d).

Ox-BisA Yield: 87%. FTIR (film,  $\text{cm}^{-1}$ ): 3060 (C–H aromatic), 2980 and 2880 (isopropylidene group), 1600 (C–C aromatic), 1240 (aromatic ether group), 1020 and 980 (oxadiazole ring).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.06 (2H, d), 7.27 (2H, d), 7.10 (2H, d), 7.00 (2H, d), 1.55 (6H, s).

## 2.2. Methods

The inherent viscosities ( $\eta_{inh}$ ) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in N-methyl-2-pyrrolidone (NMP), at a concentration of  $0.5 \text{ g dL}^{-1}$ , at  $20^\circ\text{C}$ .

The  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX 400 spectrometer, equipped with a 5 mm multinuclear inverse detection probe, operating at 400 MHz.  $^1\text{H}$  chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of the solvent (ref.  $^1\text{H}$ ,  $\text{CDCl}_3$ : 7.26 ppm).

The molecular weight was determined by gel permeation chromatography (GPC) using UV and SLS detectors and PLgel 5micro Mixed C Agilent and PLgel 5micro Mixed D Agilent Columns. Measurements

were carried out with polymer solutions in chloroform using chloroform as eluent. Polystyrene standards of known molecular weight were used for calibration.

Fourier transform infrared (FTIR) spectra were recorded on an FTIR Bruker Vertex 70 spectrometer at frequencies ranging from 400 to  $4000 \text{ cm}^{-1}$ . UV-Vis absorption spectra were obtained with a Shimadzu 3600 spectrophotometer. Steady state fluorescence emission and excitation spectra were measured with a Perkin Elmer LS55 spectrofluorimeter. Fluorescence emission and excitation spectra were recorded by exciting at the corresponding wavelengths of the absorption and emission maxima, respectively. All the solvents used were of spectrophotometric grade. Thin films for photophysical studies were prepared by casting chloroform solutions of the polymers onto glass substrates. Fluorescence lifetime and emission quantum yields were measured using an FLS 980 Edinburg Instruments spectrofluorimeter. Fluorescence lifetime measurements were carried out by the standard time-correlated single-photon counting method. The excitation was provided by an Edinburgh Picosecond Pulsed Diode Laser (EPL-375), at 375 nm. The criteria for a good fit for lifetimes were estimated by statistical parameters namely:  $\chi^2$  values close to unity and residual trace which was symmetrical about the zero axes. Fluorescence quantum yields were measured using an integrating sphere. The absorbance of the solutions was maintained around 0.1. All measurements were made at room temperature, in a quartz cuvette, with 1 cm optical path length.

## 3. Results and discussion

### 3.1. Synthesis

The polycondensation reactions were carried out at high temperature in NMP, in the presence of anhydrous potassium carbonate. The nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high performance, high temperature poly(aryl

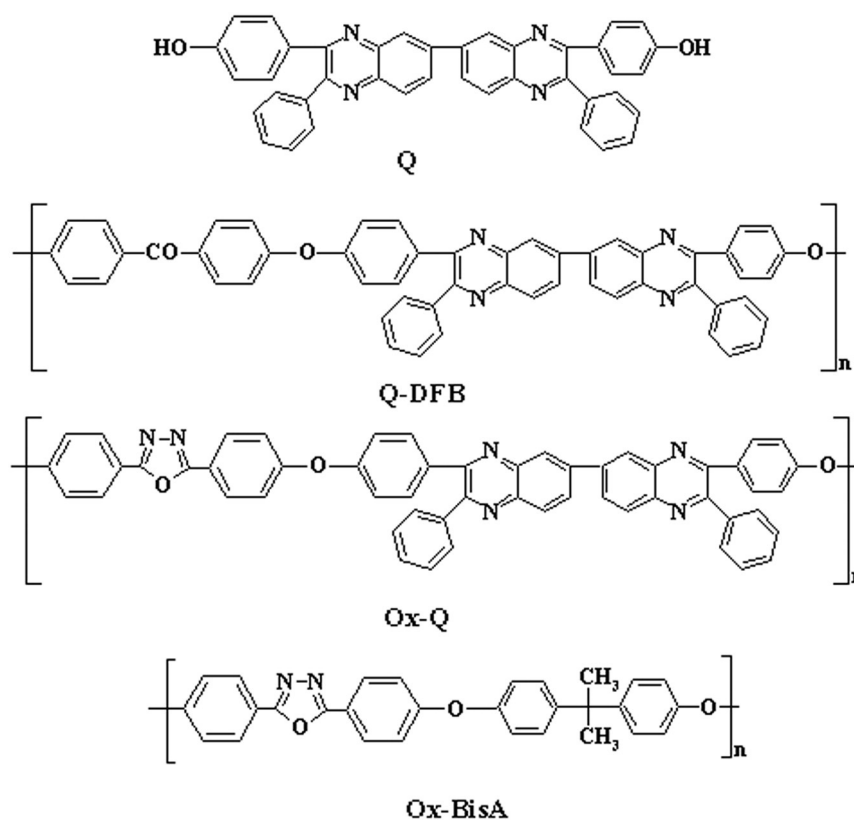


Fig. 1. Chemical structure of bis(hydroxyphenylquinoxaline), Q and polymers Q-DBF, Ox-Q and Ox-BisA.

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