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Highlights

- A new blue fluorescent diamine having a diphenyloxadiazole group was synthesized.
- Blue fluorescent polyamide and poly(amide-imide)s with pendant oxadiazole groups were prepared.
- High quantum yields and large Stokes shifts of the polymer solutions.
- Fluorescence characteristics were studied in the presence of hydrochloric acid.
- Fluorescence quenching process was observed in the presence of 2,5-dinitrophenol.

Blue light-emitting polyamide and poly(amide-imide)s

containing 1,3,4-oxadiazole ring in the side chain

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ABSTRACT

A new diamine monomer containing a 1,3,4-oxadiazole ring, 4,4'-diamino-4"-[(2-(4-phenoxy)-5-(4dimethylaminophenyl)-1,3,4-oxadiazole]-triphenylmethane, was synthesized and characterized. The diamine is used to prepare novel polyamide and poly(amide-imide)s via a polycondensation reaction with various diacid chlorides in *N*-methyl-2-pyrrolidone. The structures of the monomers and polymers are characterized by means of FTIR, ¹H-, ¹³C- and ¹⁵N NMR spectroscopy. The polymers result in high yields, and exhibit film forming ability and good solubility in many organic solvents. They show high thermal stability, with decomposition temperature being above 420 °C. The optical properties, absorption and fluorescence characteristics, in solution and solid state, are investigated. Solutions of the polymers exhibit fluorescence in the blue region, having high quantum yield in the range of 38.5-58.1%, and large Stokes shift values (110-120 nm). The introduction of hydrochloric acid into the polymer solutions has a significant effect upon the optical properties. Fluorescence quenching in the presence of 2,5-dinitrophenol was analysed using Stern-Volmer equation.

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1. Introduction

Aromatic polyamides are among the oldest members of the class of thermally stable polymers. They have received considerable attention with regard to the production of high performance materials, due to their outstanding thermal stability, chemical resistance, and electrical and mechanical properties [1,2]. However, their high glass transition temperature and limited solubility in organic solvents make their processability quite difficult. To overcome these drawbacks to some degree an attractive synthetic approach is the incorporation of bulky substituents such as pendant groups along the polymer backbone [3]. In many cases, the introduction into the macromolecular chains of polyamides of various heterocycles including imide and 1,3,4-oxadiazole rings together with flexible groups led to polymers exhibiting a combination of remarkable properties and processability, particularly in thin films and coatings [4,5].

Heterocyclic polymers containing 1,3,4-oxadiazole rings in the main chain or in the side chain are well known for their high thermal resistance in oxidative atmosphere, good hydrolytic stability, low dielectric constant and tough mechanical properties that make them good candidates for various applications such as high temperature fibers, reinforced materials and membranes for gas separation [6-10]. Particularly interesting are the properties determined by the electronic structure of the 1,3,4oxadiazole ring because it is characterized by high electron affinity. Due to their electronwithdrawing character which facilitates the injection and transport of electrons, such polymers can be used as promising electron-transporting materials in light-emitting and electronic memory devices [11-15]. The external quantum efficiency in electroluminescence devices with p-conjugated

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polymers, polymers with isolated chromophores and dye-dispersed polymer films can be improved by the introduction of oxadiazole derivative layers between an emissive layer and the cathode of organic light-emitting diodes [16].

Much research is made in developing blue light-emitting polymer materials with high thermal stability and high emission efficiency. A blue light-emitting device can generate all colors by using the appropriate dyes, in comparison with green or red which cannot emit blue light in this way [17]. One approach to develop such structures is the introduction in the main chain or in the side chain of the chromophore segments which emit blue light. Polymers with a well defined conjugation length can be obtained, which is highly desired, taking into account that a larger distribution of conjugation length leads to a larger broadness of the emission bands [17-21].

Among the efficient organic luminophors 2,5-diphenyl-substituted-1,3,4-oxadiazoles are known to emit light in the blue region. This can be explained by the effect of the 1,3,4-oxadiazole ring which is close to that of *p*-phenylene group in a conjugated aromatic system [22]. 2,5-Diaryl-1,3,4-oxadiazoles are similar to polyphenyl hydrocarbons with the corresponding number of aromatic nuclei. Electron donor substituents like *p*-dimethylamino group can significantly raise the fluorescence intensity in comparison with electron acceptor substituents. Also, the incorporation of electron donor substituents in the structure of 2,5-diaryl-substituted oxadiazoles gives large absorption shifts and photoluminescence spectra toward longer wavelength, as well as a greater Stokes shift [23].

From previous investigations it was concluded that certain polymers containing dimethylamino substituents in the *para*-position of the pendant chromophoric 2,5-diphenyl-1,3,4-oxadiazole unit are promising candidates for emissive materials in light-emitting devices [24]. The substituted diphenyl-1,3,4-oxadiazole units are able to transport holes as well as electrons and show an intense fluorescence. Thus, in our laboratory were developed poly(1,3,4-oxadiazole-ether-imide)s [25,26], poly(1,3,4-oxadiazole-imide)s [27] and poly(1,3,4-oxadiazole-ester-imides) [28] which were

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synthesized by a polycondensation reaction of 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole with certain aromatic dianhydrides, such as 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4dicarboxyphenoxy)phenyl]propane dianhydride, 2,2'-bis-[(3,4-dicarboxyphenoxy)phenyl]-1,4phenylenediisopropylidene dianhydride, bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride, and 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate) dianhydride. The obtained polymers exhibited fluorescence in the blue region when excited with UV light. The presence of the heteroatom with a free electron pair, in this case the nitrogen atoms in the oxadiazole rings and dimethylamino groups, gives the opportunity for protonation with hydrochloric acid (HCl) that may change the optical properties [29].

In this paper we describe the synthesis and characterization of a new diamine containing 1,3,4oxadiazole ring, 4,4'-diamino-4"-[(2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,5-oxadiazole]triphenylmethane. Novel polyamide and poly(amide-imide)s were prepared by polycondensation reaction of the new diamine with various diacid chlorides. The properties of the resulting polymers, such as solubility, thermal and optical characteristics were investigated. The polymers exhibited high thermal stability and pure blue light emission.

2. Experimental

2.1. Materials

4-Dimethylaminobenzhydrazide, **1**, 4-fluorobenzoyl chloride, **2**, 4-hydroxybenzaldehyde, terephthalic acid, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4-aminobenzoic acid, 4-bromo-*o*-xylene, dimethyldichlorosilane, aniline, aniline hydrochloride, phosphorus oxychloride (POCl₃), potassium carbonate (K₂CO₃), thionyl chloride, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-

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dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and pyridine were provided from Aldrich and used as received.

2.2. Characterization

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). The inherent viscosity (η_{inh}) of the polymers was determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20 °C, at a concentration of 0.5 g dL⁻¹. 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 DMF by using DMF as eluent. Polystyrene standards of known molecular weight were used for calibration. FTIR spectra were recorded on a Bruker Vertex 70 at frequencies ranging from 400 to 4000 cm⁻¹ using KBr pellets or films. The NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.1, 100.6 and 40.6 MHz for ¹H, ¹³C, and ¹⁵N nuclei, respectively. Samples were recorded with either a 5 mm multinuclear inverse detection z-gradient probe (¹H spectra and all H-C/H-N 2D experiments) or with a 5 mm four nuclei direct detection z-gradient probe (¹³C spectra). All the experiments were recorded using standard pulse sequences, in the version with z-gradients for 2D spectra, as delivered by Bruker with TopSpin 2.1 PL6 spectrometer control and processing software. Chemical shifts are reported in δ units (ppm) and were referenced to the internal deuterated solvent for ¹H and ¹³C chemical shifts (DMSO referenced at ¹H: 2.51 ppm and ¹³C: 39.47 ppm) and referenced to liquid ammonia (0.0 ppm) using nitromethane (380.2 ppm) as external standard for ¹⁵N chemical shifts. Atomic Force Microscopy (AFM) images were taken in air, on a SPM SOLVER Pro-M instrument. A NSG10/Au Silicon tip with a 35 nm radius of curvature and 255 kHz oscillation mean frequency was used. The apparatus was operated in semi-contact mode, over a $2x2 \ \mu m^2$ scan area,

256x256 scan point size images being thus obtained. Thermogravimetric analysis (TGA) was carried out in nitrogen, at a heating rate of 10 °C min⁻¹, using a Mettler Toledo TGA/SDTA 851^e balance. The heating scans were performed on 2 to 5 mg of sample in the temperature range of 25-900 °C. Alumina crucible (70 μ L) is used as sample holder. The initial decomposition temperature is characterized as the temperature at which the sample achieves 5% weight loss. The temperature of 10% weight loss (T_{10}) and the temperature of maximum decomposition rate which is the maximum signal in differential thermogravimetry (DTG) curves were also recorded. Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of Stare software. The samples were encapsulated in aluminum pans having pierced lids to allow escape of volatiles. The heating rate of 10 °C min⁻¹ and nitrogen purge at 120 mL min⁻¹ was employed. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. UV-Vis absorption and photoluminescence (PL) spectra were recorded with a Analytik Jena - Specord 200 spectrophotometer and a Perkin-Elmer LS55 luminescence spectrofluorimeter, respectively. All solvents used in the present paper were spectrophotometric grade. Quenching studies were carried out by adding small amounts of the quencher (3,5-dinitrophenol) to the studied polymer in DMAc solution. PL spectra were recorded after each addition. All measurements were performed at room temperature. For PL measurements polymer films were prepared by using 1% polymer solutions in NMP, which were spin-coated on quartz slides at about 1000 rpm, for 30 s, at room temperature.

2.3. Synthesis

2.3.1. N-(4-dimethylaminobenzoyl)-N'-(4-fluorobenzoyl)hydrazine (3)

4-Dimethylaminobenzhydrazide (8.95 g, 0.05 mol), NMP (65 mL) and pyridine (4.0 mL) were placed in a 100 mL three-necked flask equipped with mechanical stirrer, and the mixture was stirred

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until complete dissolution was achieved. The solution was cooled to 0 °C, and 4-fluorobenzoyl chloride (7.925 g, 0.05 mol) was added under stirring. The flask content was maintained at 0 °C for 1 h and at room temperature for 6 h. The reaction mixture was poured into water while stirring, and the resulting precipitate was filtered, washed with water and dried.



Yield: 13.50 g (89.7 %). Mp: 238-240°C. FTIR (KBr, cm⁻¹): 3321 (NH), 2895 (C-H aromatic), 1680 and 1636 (C=O), 1604, 1507 (C-C aromatic). ¹H NMR (400 MHz, DMSO-d₆, δ): 2.99 (6H, s, CH₃), 6.75 (2H, d, 8.8 Hz, H-2), 7.37 (2H, t, 8.8 Hz, H-9), 7.82 (2H, d, 8.4 Hz, H-3), 8.01 (2H, dd, 5.6, 8.0 Hz, H-8), 10.15 (1H, s, NH-4), 10.40 (1H, s, NH-6). ¹³C NMR (100 MHz, DMSO-d₆, δ): 39.65 (2C, CH₃), 110.80 (2C, C-2), 115.46 (2C, d, ²J_{C-F} = 22 Hz, C-9), 118.86 (1C, C-4), 128.87 (2C, C-3), 129.25 (1C, d, ⁴J_{C-F} = 3 Hz, C-7), 130.1 (2C, d, ³J_{C-F} = 9 Hz, C-8), 152.45 (1C, C-1), 164.13 (1C, d, ¹J_{C-F} = 249 Hz, C-10), 164.91 (1C, CO-6), 165.75 (1C, CO-5). ¹⁵N NMR (40 MHz, DMSO-d₆, δ): 52.3 (N), 118.8 (NH-5), 122.4 (NH-6). Anal. calcd. for C₁₆H₁₆O₂N₃F₁: C 63.78, H 5.31, N 13.55; found: C 63.49, H 5.62, N 13.38.

2.3.2. 2-(4-Dimethylaminophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole (4)

N-(4-dimethylaminobenzoyl)-N'-(4-fluorobenzoyl)hydrazine, **3**, (12 g) and POCl₃ (150 mL) were introduced into a flask equipped with magnetic stirrer, and refluxed for 6 h. After cooling to room temperature, the reaction mixture was poured into an ice-water mixture, and the resulting precipitate was filtered, washed several times with water and dried.



Yield: 10 g (88.3 %). Mp: 161-165°C. FTIR (KBr, cm⁻¹): 3063 (C-H aromatic), 2890, 2812 (C-H aliphatic), 1611, 1493 (-C-C- aromatic), 1010, 989 (1,3,4-oxadiazole ring). ¹H NMR (400 MHz, DMSO-d₆, δ): 3.03 (6H, s, CH₃), 6.86 (2H, d, 9.2 Hz, H-2), 7.47 (2H, t, 8.8 Hz, H-9), 7.91 (2H, d, 8.8 Hz, H-3), 8.15 (2H, dd, 5.4, 8.8 Hz, H-8). ¹³C NMR (100 MHz, DMSO-d₆, δ): 39.60 (2C, CH₃), 109.56 (1C, C-4), 111.70 (2C, C-2), 116.55 (2C, d, ²J_{C-F} = 22 Hz, C-9), 120.36 (1C, d, ⁴J_{C-F} = 3 Hz, C-7), 127.91 (2C, C-3), 129.0 (2C, d, ³J_{C-F} = 9 Hz, C-8), 152.31 (1C, C-1), 162.04 (1C, C-6), 163.86 (1C, d, ¹J_{C-F} = 249 Hz, C-10), 164.66 (1C, C-5). ¹⁵N NMR (40 MHz, DMSO-d₆, δ): 54.8. Anal. calcd. for C₁₆H₁₄O₁N₃F₁: C 67.64, H 4.94, N 14.84; found: C 67.35, H 5.12, N 14.58.

2.3.3. 4,4'-Diamino-4"-hydroxy-triphenylmethane (5)

4-Hydroxybenzaldehyde reacted with aniline in the presence of an acid catalyst (aniline hydrochloride) to give diamine **5**, according to a published procedure [30].

Yield: 31%. Mp: 202-203 °C. FTIR (KBr, cm⁻¹): 3382 and 3321 (NH-amine), 2855 (C-H aliphatic). ¹H-NMR (400 MHz, DMSO-d₆, δ): 4.86 (4H, bs, NH₂), 5.05 (1H, s, CH), 6.45 (4H, d, 8.4 Hz), 6.64 (2H, d, 8.4 Hz), 6.70 (4H, d, 8.4 Hz), 6.84 (2H, d, 8.4 Hz), 9.14 (1H, s, OH).

2.3.4. 4,4'-Diamino-4"-[(2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,5-oxadiazole]triphenylmethane (6)

The diamine containing 1,3,4-oxadiazole ring **6** was prepared by the reaction of 2-(4dimethylaminophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole, **4**, with 4,4'-diamino-4"-hydroxytriphenylmethane, **5**, in the presence of K₂CO₃, in NMP as solvent. In a 100 mL round-bottom flask fitted with magnetic stirrer, Dean-Stark trap, and nitrogen inlet and outlet, were placed **4** (2.83 g, 0.01 mol), **5** (2.90 g, 0.01 mol), anhydrous K₂CO₃ (1.52 g, 0.011 mol), NMP (23 mL), and toluene

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(15 mL). The mixture was heated at 140 °C for 3 h, and then the toluene was distilled off under vacuum. The reaction mixture was further heated at 140 °C for 17 h, with stirring, under nitrogen. It was cooled to room temperature, poured into water, and the resulting solid was filtered, washed several times with water and dried. The product was purified by treatment with 35% HCl until a clear solution was obtained, which was filtered and further precipitated with 10% NaOH solution. The resulting diamine **6** was filtered, washed with water and dried.



Yield: 3.9 g (70.5 %). Mp: 205-207 °C. FTIR (KBr, cm⁻¹): 3436 (NH₂ asymmetric stretching), 3350 (NH₂ symmetric stretching), 3030 (C-H aromatic), 2890, 2890 (C-H aliphatic), 1611, 1508 (C-C in aromatic rings), 1241 (C-O-C), 1013, 956 (1,3,4-oxadiazole ring). ¹H NMR (400 MHz, DMSO-d₆, δ): 3.00 (6H, s, CH₃), 4.93 (4H, bs, NH₂), 5.22 (1H, s, H-5), 6.52 (4H, d, 8 Hz, H-2), 6.78 (4H, d, 8 Hz, H-3), 6.83 (2H, d, 8.8 Hz, H-18), 7.03 (2H, d, 8 Hz, H-8), 7.14 (4H, d, 8 Hz, H-7 and H-11), 7.87 (2H, d, 8.8 Hz, H-17), 8.05 (2H, d, 8.4 Hz, H-12). ¹³C NMR (100 MHz, DMSO-d₆, δ): 39.56 (2C, CH₃), 53.92 (1C, C-5), 109.71 (1C, C-16), 111.68 (2C, C-18), 113.76 (4C, C-2), 118.07 (2C, C-11), 118.11 (1C, C-13), 119.29 (2C, C-8), 127.79 (2C, C-17), 128.45 (2C, C-12), 129.3 (4C, C-3), 130.49 (2C, C-7), 131.75 (2C, C-4), 142.07 (1C, C-6), 146.62 (2C, C-1), 152.20 (1C, C-19), 152.94 (1C, C-9), 159.91 (1C, C-10), 162.43 (1C, C-14), 164.35 (1C, C-15). ¹⁵N NMR (40 MHz, DMSO-d₆, δ): 54.9 (N), 57.15 (NH₂). Anal. calcd. for C₃₅H₃₁O₂N₅: C 75.54, H 5.60, N 12.65; found: C 75.38, H 5.53, N, 13.31.

2.3.5. Terephthaloyl chloride (7a)

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Terephthaloyl chloride was prepared by refluxing the terephthalic acid with excess of thionyl chloride. It was purified by recrystallization from chloroform. Mp: 79-80°C

2.3.6. 2,2-Bis[N-chloroformylphenyl)phthalimidyl]hexafluoropropane (7b) and 2,2-bis[N-chloroformylphenyl)phthalimidyl]dimethylsilane (7c)

These compounds were obtained by treating with thionyl chloride the corresponding dicarboxylic acids resulting from the condensation reaction of *p*-aminobenzoic acid with 4,4'- (hexafluoroisopropylidene)diphthalic anhydride and bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride, respectively, in glacial acetic acid as a solvent and dehydrating reagent, at reflux temperature [31,32]. Bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride was prepared by a multistep reaction, following a published method, starting from the reaction of 4-bromo-*o*-xylene with dimethyldichlorosilane to produce bis(3,4-dicarboxyphenyl)dimethylsilane; the further oxidation with potassium permanganate resulted in bis(3,4-dicarboxyphenyl)dimethylsilane which by dehydration in refluxing acetic anhydride gave the corresponding dianhydride [33].

7b. Mp: 311-313 °C [31]. FTIR (KBr, cm⁻¹): 1780 (C=O of imide ring and COCl), 1720 (C=O of imide ring), 1600 (aromatic), 1390 (C-N), 1210 and 1180 (C-F), 1100 and 720 (imide ring). ¹H NMR (400 MHz, DMSO-d₆, δ): 7.61 (4H, d, 8.8 Hz), 7.77 (2H, bs), 7.99 (2H, d, 8 Hz), 8.10 (4H, d, 8.4 Hz), 8.22 (2H, d, 8 Hz).

7c. Mp: 218-222 °C [32]. FTIR (KBr, cm⁻¹): 1780 (C=O of imide ring and COCl); 1730 (C=O of imide ring); 1375 (C-N); 740 (imide ring) and 1220 and 820 (methyl-silane bonds). ¹H NMR (400 MHz, DMSO-d₆, *δ*): 0.79 (6H, s, CH₃), 7.60 (4H, d, 8.4 Hz), 8.00 (2H, d, 7.2 Hz), 8.09 (4H, d, 8.8 Hz), 8.13 (2H, d, 7.6 Hz), 8.15 (2H, bs).

2.3.7. Model compound (8)

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Synthesis of model compound **8** was performed by solution condensation reaction of diamine **6** with benzoyl chloride, in the presence of pyridine as acid acceptor. In a 50 mL three-necked flask equipped with mechanical stirrer, and nitrogen inlet and outlet, were placed diamine **6** (0.94 g, 1.7 mmol), NMP (7 mL) and pyridine (0.27 mL) and the mixture was stirred under nitrogen until complete dissolution. The solution was cooled to -10 °C and benzoyl chloride (0.478 g, 3.4 mmol) was added with rapid stirring. The flask content was stirred below 0 °C for 20 min and at room temperature for 6h. Then the solution was precipitated by pouring into water. The precipitated product was filtered, washed with water and twice with ethanol under stirring, and dried under vacuum at 110 °C for 4 h.



Yield: 1.2 g (93 %). Mp: 172-174 °C. FTIR (KBr, cm⁻¹): 3300 (NH stretching), 3030 (aromatic C-H), 2887, 2808 (aliphatic C-H), 1655 (C=O of amide), 1612, 1489 (aromatic -C-C-), 1243 (aromatic ether), 1015 and 945 (1,3,4-oxadiazole ring). ¹H NMR (400 MHz, DMSO-d₆, *δ*): 3.00 (6H, s, CH₃), 5.62 (1H, bs,H-15), 6.84 (2H, d, 7.9 Hz, H-2), 7.10-7.24 (10H, m, H-9, H-12, H-13, H-17), 7.53-7.59 (6H, m, H-23 and H-24), 7.78 (4H, d, 7.60 Hz, H-18), 7.89 (2H, d, 8.00 Hz, H-3), 7.97 (4H, d, 6.60 Hz, H-22), 8.08 (2H, d, 7.9 Hz, H-8), 10.28 (2H, bs, NH). ¹³C NMR (400 MHz, DMSO-d₆, *δ*): 39.56 (2C, CH₃), 53.18 (1C, C-5), 109.72 (1C, C-4), 111.68 (2C, C-2), 118.26 (2C, C-9), 119.56 (2C, C-12), 120.40 (4C, C-18), 127.60 (4C, C-22), 127.80 (2C, C-3), 128.31 (4C, C-23), 128.49 (2C, C-8), 129.08 (2C, C-17), 130.67 (2C, C-13), 131.47 (2C, C-24), 134.93 (2C, C-11), 139.74 (2C, C-19), 139.14 (2C, C-16), 140.30 (1C, C-14), 152.21 (1C, C-1), 153.48 (1C, C-11), 159.74

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(1C, C-10), 162.42 (1C, C-6), 164.38 (1C, C-5), 165.44 (2C, CO). ¹⁵N NMR (400 MHz, DMSO-d₆,
δ): 56.1 (N), 129.0 (NH).

2.3.8. Synthesis of the polymers (9)

The polymers **9** were synthesized by a solution polycondensation reaction of equimolecular amounts of diamine **6** with diacid chlorides **7**, in NMP as a solvent and in the presence of pyridine as acid acceptor. In a typical experiment, polymer **9b** was prepared as follows: in a 100 mL three-necked flask equipped with mechanical stirrer, and nitrogen inlet and outlet, were placed diamine **6** (1.106 g, 0.002 mol), NMP (20 mL) and pyridine (0.32 mL) and the mixture was stirred under nitrogen until complete dissolution. The solution was cooled to -10 °C and diacid chloride **7b** (1.438 g, 0.002 mol) was added with rapid stirring. The content of the flask was kept below 0 °C for 15 min. The cooling bath was then removed and the reaction mixture was allowed to reach room temperature after which it was stirred for another 4 h to yield a viscous polymer solution. The solution was diluted to about 5% by addition of more NMP and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with ethanol under stirring, and dried under vacuum at 110 °C for 5 h to give the polymer **9b**.

Flexible transparent free standing films were obtained by casting onto glass plates 10% polymer solutions of **9a**, **9b** and **9c** followed by heating at 100, 130, 160, 190 and 220 °C, each for 30 min, to evaporate the solvent. The films were stripped off the plate by immersion in hot water for 2 h. Films prepared from polymer **9a** were brittle.

Polymer **9a**



Yield: 91%. FTIR (KBr, cm⁻¹): 3334 (NH stretching), 3032 (aromatic C-H), 2919, 2855, 2804 (aliphatic C-H), 1664 (C=O of amide), 1611, 1508 (aromatic -C-C-) 1240 (aromatic ether), 1016 and 944 (1,3,4-oxadiazole ring). ¹H NMR (400 MHz, DMSO-d₆, δ): 3.02 (6H, s, CH₃), 5.64 (1H, s, H-15), 6.84 (2H, bs, H-2), 7.12-7.23 (10H, m, H-9, H-12, H-13, H-17), 7.77 (4H, bs, H-18), 7.88 (2H, bs, H-3), 8.07-8.09 (6H, m, H-8, H-22, H-23), 10.42 (2H, bs, NH). ¹³C NMR (100 MHz, DMSO-d₆, δ): 39.58 (2C, CH₃), 54.16 (1C, C-15), 109.70 (1C, C-4), 111.70 (2C, C-2), 118.28 (2C, C-9), 119.58 (2C, C-12), 120.50 (4C, C-18), 127.65 (4C, C-22 and C-23), 127.81 (2C, C-3), 128.51 (2C, C-8), 129.13 (4C, C-17), 130.68 (2C, C-13), 137.20 (2C, C-19), 137.37 (1C, C-24), 139.37 (2C, C-6), 140.24 (1C, C-14), 152.23 (1C, C-1), 153.30 (1C, C-11), 159.73 (1C, C-10), 162.42 (1C, C-6), 162.42 (1C, C-5), 164.68 (2C, C-20). ¹⁵N NMR (40 MHz, DMSO-d₆, δ): 54.9 (N), 128.3 (CONH).

Polymer 9b



Yield: 94%. FTIR (KBr, cm⁻¹): 3340 (NH stretching), 3065 (aromatic C-H), 2887, 2808 (aliphatic C-H), 1785 and 1724 (C=O of imide ring), 1673 (C=O of amide), 1610, 1507 (aromatic -C-C-), 1367 (C-N stretching of imide) 1242 (aromatic ether), 1017 and 962 (1,3,4-oxadiazole ring), 718 (C=O bending of imide ring). ¹H NMR (400 MHz, DMSO-d₆, *δ*): 3.01 (6H, s, CH₃), 5.64 (1H, s, H-15), 6.84 (2H, bs, H-2), 7.13-7.22 (10H, m, H-9, H-12, H-13 and H-17), 7.62 (4H, bs, H-23), 7.78 (6H, bs, H-18 and H-28), 7.87 (2H, bs, H-3), 8.00 (2H, bs, H-30), 8.08 (6H, bs, H-8 and H-22), 8.21 (2H, bs, H-31), 10.38 (2H, bs, NH). ¹³C NMR (100 MHz, DMSO-d₆, *δ*): 39.8 (2C, CH₃), 54.14 (1C,

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C-15), 64.34 (1C, C-33), 109.71 (1C, C-4), 111.73 (2C, C-2), 118.29 (2C, C-9), 119.61 (2C, C-12), 120.33 (4C, C-18), 123.71 (2C, C-28), 124.49 (2C, C-31), 127.03 (4C, C-23), 127.83 (2C, C-3), 128.29 (4C, C-22), 128.54 (2C, C-8), 129.17 (4C, C-17), 130.71 (2C, C-13), 132.57 (2C, C-32), 132.99 (2C, C-27), 134.32 (2C, C-24), 134.72 (2C, C-21), 135.91 (2C, C-30), 137.38 (4C, C-19 and C-29), 139.29 (2C, C-16), 140.31 (1C, C-14), 152.27 (1C, C-1), 153.51 (1C, C-11), 159.78 (1C, C-10), 162.46 (1C, C-6), 164.40 (1C, C-5), 164.91 (2C, C-20), 165.74, 165.88 (4C, C-25 and C-26). 15 N NMR (40 MHz, DMSO-d₆, δ): 55.6 (N), 127.3 (CONH).

Polymer 9c



Yield: 92%. FTIR (KBr, cm⁻¹): 3354 (NH stretching), 3052 (aromatic C-H), 2880, 2808 (aliphatic C-H), 1773 and 1720 (C=O of imide ring), 1670 (C=O of amide), 1610, 1507 (aromatic -C-C-), 1366 (C-N stretching of imide) 1240 (aromatic ether), 1017 and 960 (1,3,4-oxadiazole ring), 810 (methylsilane), 718 (C=O bending of imide ring). ¹H NMR (400 MHz, DMSO-d₆, δ): 0.79 (6H, s, CH₃-Si), 3.01 (6H, s, CH₃), 5.64 (1H, s, H-15), 6.84 (2H, bs, H-2), 7.13-7.22 (10H, m, H-9, H-12, H-13 and H-17), 7.61 (4H, bs, H-23), 7.77 (4H, bs, H-18), 7.87 (2H, bs, H-3), 8.00 (2H, bs, H-31), 8.06-8.14 (12H, m, H-8, H-22, H-28 and H-30), 10.35 (2H, bs, NH). ¹³C NMR (100 MHz, DMSO-d₆, δ): -3.39 (2C, CH₃-Si), 40.11 (2C, CH₃), 54.11 (1C, C-15), 109.69 (1C, C-4), 111.67 (2C, C-2), 118.25 (3C, C-7 and C-9), 119.50 (2C, C-12), 120.28 (4C, C-18), 122.67 (2C, C-31), 126.82 (2C, C-23), 127.75 (2C, C-3), 128.11 (6C, C-8 and C-22), 128.34 (2C, C-28), 129.07 (4C, C-17), 130.62 (2C, C-13), 130.73 (2C, C-27), 132.45 (2C, C-32), 134.34 (2C, C-21), 134.49 (2C, C-24), 137.28 (2C, C-19), 139.19 (2C, C-16), 140.24 (3C, C-14 and C-30), 145.63 (2C, C-29), 152.21 (1C, C-1),

153.47 (1C, C-11), 159.70 (1C, C-10), 162.38 (1C, C-6), 164.32 (1C, C-5), 164.81 (2C, C-20), 166.60 (2C, C-26), 166.83 (2C, C-25). ¹⁵N NMR (40 MHz, DMSO-d₆, δ): 55.9 (N), 127.7 (CONH).

3. Results and discussion

3.1. Synthesis of diamine 6

A new diamine **6** was prepared through a sequence of reactions as shown in scheme 1. 4-Dimethylaminobenzhydrazide, **1**, reacted with *p*-fluorobenzoyl chloride, **2**, in NMP as solvent and pyridine as catalyst to give N-(4-dimethylaminobenzoyl)-N'-(4-fluorobenzoyl)hydrazine, **3**. The cyclodehydration of **3** with POCl₃ gave the corresponding 1,3,4-oxadiazole derivative 2-(4dimethylaminophenyl)-5-(4-fluorophenyl)-1,3,4-oxadiazole, **4**. The diamine **6** was prepared by nucleophilic substitution reaction of fluorinated compound **4** with 4,4'-diamino-4"hydroxytriphenylmethane, **5**, in NMP, in the presence of K₂CO₃ as catalyst, at high temperature. This method is based on the nucleophilic displacement of the activated fluorine substituent by potassium phenoxide, in polar aprotic solvents such as DMAc or NMP. The oxadiazole moiety can accept a negative charge and lower the activation energy for the displacement of the *p*-substituted fluorine group through a Meinsenheimer complex, analogous to conventional activating group such as ketone or sulfone [34].

Scheme 1

The structure of intermediate compounds **3**, **4** and **5** and of diamine **6** was confirmed by FTIR and ¹H-, ¹³C- and ¹⁵N NMR spectroscopy. All the spectra were in good agreement with the proposed molecular structures. In FTIR spectrum of diamine **6** characteristic absorption bands of the functional groups appeared at 3430 and 3334 (NH asymmetric and symmetric stretching), 1241

and 1165 cm⁻¹ (-C-O-C stretching), 1012 and 960 cm⁻¹ (=C-O-C= stretching in oxadiazole ring) confirming the presence of primary amine groups, aromatic ether linkage and 1,3,4-oxadiazole ring.

The chemical structure of the synthesized compounds was also confirmed by NMR spectroscopy. Unambiguous assignments for ¹H-, ¹³C- and ¹⁵N chemical shifts were based on twodimensional homo- and heteronuclear correlations like ¹H, ¹H-COSY (Correlation Spectroscopy), ¹H.¹³C and ¹H.¹⁵N HSOC (Heteronuclear Single Ouantum Coherence) as well as HMBC (Heteronuclear Multiple Bond Coherence). The ¹H-, ¹³C- and ¹H, ¹³C-HSOC NMR spectra corresponding to diamine 6 are presented in Fig. 1. The assignments of the 1 H and 13 C chemical shifts were made according to the numbering presented in experimental part. The J-coupled protons were assigned from the ¹H, ¹H-COSY spectrum (not shown) while the carbons from CH groups were assigned from the ¹H.¹³C-HSOC spectrum. The quaternary carbons were identified from the ¹H,¹³C-HMBC spectrum (not shown). The ¹⁵N chemical shifts were obtained as projections from the 2D ¹H,¹⁵N-HSQC and ¹H,¹⁵N-HMBC spectra. The chemical shifts of the nitrogen atoms from the oxadiazole ring could not be determined because there were no protons within two or three bond distances. In the ¹H NMR spectrum of **6** the primary aromatic amine protons appeared at 4.93 ppm as a singlet and the protons in *ortho* position to the amine groups H-2 appeared as doublet at 6.52 ppm. The 13 C NMR spectrum of 6 showed signals which resonated in the region of 39.6-164.4 ppm. In the ¹⁵N NMR spectrum of 6 characteristic peaks appeared at 54.9 ppm due to the presence of dimethylamino groups and at 57.15 ppm due to the presence of amino groups. All these results demonstrated that the diamine monomer $\mathbf{6}$ was successfully prepared.

Figure 1

3.2. Synthesis and general characterization of model compound 8 and polymers 9

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The model compound **8** was synthesized by condensation reaction of diamine **6** with benzoyl chloride. The polyamide **9a** was prepared by low-temperature solution polycondensation reaction of diamine **6** with terephthaloyl chloride, **7a**, in NMP as solvent and with pyridine as the acid acceptor. Poly(amide-imide)s **9b** and **9c** were prepared by the same method starting from diamine **6** and two diacid chlorides containing preformed imide rings **7b** and **7c** (Scheme 2). The polycondensation proceeded homogenously during the reaction and afforded clear, viscous polymer solutions.

Scheme 2

The structures of model compound **8** and polymers **9** were identified by FTIR and NMR spectroscopy. In the FTIR spectra of **8** and **9** characteristic absorption band appeared at around 1670 cm⁻¹ due to carbonyl stretching vibration of amide groups. The band at about 1240 cm⁻¹ appeared because of the absorption of the aromatic ether linkage of the pendant segments coming from diamine **6**. The absorption bands appearing at around 1017 and 940 cm⁻¹ were assigned to oxadiazole rings while the bands appearing at 2919 and 2855 cm⁻¹ were characteristic of aliphatic groups. Characteristic bands at 3070 and 1602 cm⁻¹ were due to aromatic C-H stretching and aromatic C-C stretching, respectively. In the FTIR spectra of **9b** and **9c** the strong bands appearing at 1785 and 1725 cm⁻¹ were attributed to asymmetrical and symmetrical stretching vibrations of carbonyl groups of imide rings while the characteristic absorption band at 740 cm⁻¹ was due to imide ring deformation. Polymer **9b** exhibited absorption bands at 1180 and 1210 cm⁻¹ due to the presence of hexafluoroisopropylidene groups (C-F stretching). In the case of polymer **9c** containing dimethylsilane groups a characteristic absorption band appeared at 810 cm⁻¹ (Si-C stretching).

Fig. 2 illustrates the ¹H- and ¹³C NMR spectra of polyamide **9a**. The assignments of the ¹H and ¹³C chemical shifts were made according to the numbering presented in experimental part and they were based on 2D NMR experiments. The NMR data provided evidence for the formation of the amide group. In ¹H NMR spectrum of **9a**, the peak corresponding to amide protons is shifted downfield as compared to the peak corresponding to amine protons from the diamine **6**. In ¹⁵N

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NMR spectrum of **9a** characteristic peak for amide groups appeared at 128.3 ppm confirming the formation of polyamide during polycondensation reaction.

Figure 2

The solubility of the polymers **9** was tested qualitatively in various organic solvents. All the polymers were easily soluble at room temperature in polar aprotic solvents, such as NMP, DMAc, N,N-dimethylformamide and DMSO. The good solubility of polyamide **9a** was due to the presence of voluminous pendant segments 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole which prevented the macromolecular chains from packing into tight structure through hydrogen bonding between amide groups and led to decreased chain-chain interactions, thus allowing the solvent to penetrate among polymer chains. In the case of poly(amide-imide)s **9b** and **9c** the presence of hexafluoroisopropylidene or dimethylsilane units contributed even more to an increase of the solubility. The inherent viscosity values of polymers **9** were in the range of 0.26–0.53 dL g⁻¹ (Table 1).

The molecular weight of polymers was determined by GPC. The data of molecular weights are collected in table 1. The number-average molecular weight (M_n) was in the range of 16100-32100 g mol⁻¹, the weight-average molecular weight (M_w) was in the range of 20800-42300 g mol⁻¹, and the polydispersity (M_w/M_n) was in the range of 1.29-1.44.

Table 1

The polymers **9** showed film forming ability. Their solutions in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield films having a thickness of 20-50 μ m. Free standing flexible films were obtained only in the case of poly(amide-imide)s **9b** and **9c**. The films of **9a** were brittle, probably due to a higher rigidity and lower molecular weight of the polymer. Very thin films were prepared from diluted NMP solutions (concentration 2%) by spin coating onto silicon wafers. The quality of such films as deposited on substrates was studied by

atomic force microscopy (AFM). 2D and 3D AFM images of polymer film surface **9a** are shown in Fig. 3.

Figure 3

It can be seen that the film exhibited compact and homogeneous surface, without pinholes or cracks. The scanning rate of $2x2 \ \mu m$ was used to evaluate the root mean square (RMS) roughness. The RMS of the films was in the range of 4-6 Å being of the same order of magnitude as that of neat highly polished silicon wafers which were used as substrates. It means that the present films are very smooth, practically defectless. These qualities are required when such films are used in microelectronic devices.

A glass transition temperature was not observed from DSC measurements up to 350 °C. The presence of voluminous pendant segments of (2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,5-oxadiazole) and other aromatic moieties in the main chain hindered the segmental movement of the polymer chain which resulted in a glass transition temperature higher than the limit of DSC measurements.

The thermal stability was investigated by thermogravimetric analysis (TGA). Fig. 4 illustrates the TG and DTG curves of polymers **9**. As expected, these polymers showed excellent thermal stability, with insignificant weight loss up to 400 °C. The temperatures of 5% (T_5) and 10% (T_{10}) weight losses were in the range of 423-433 °C and 455-473 °C, respectively. The polymers showed high char yield at 700 °C, in the range of 50.4-53.7%. It can be seen that the values of T_5 and T_{10} of poly(amide-imide)s **9b** and **9c** were similar to those of polyamide **9a** suggesting that the introduction of imide rings did not improve to a great extent the thermal stability. This can be explained by the presence in the polymer structure of amide linkages which decompose at lower temperature and can determine the initial decomposition temperature [35]. As it can be seen from DTG curves the degradation process of **9b** and **9c** exhibited two maxima of decomposition. The first (T_{maxI}) was in the range of 494-538 °C and was due to the destruction of amide groups more

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sensitive to thermal degradation, oxadiazole rings and ether linkages. The second maximum of decomposition (T_{max2}) was in the range of 556-609 °C and was due to the degradation of polymer chain itself. Polymer **9a** without imide rings exhibited only one maxima of decomposition at 511 °C (Table 1).

Figure 4

3.3. Optical properties of 6, 8 and 9

The optical properties of diamine **6**, model compound **8** and polymers **9** were analysed by UVvis and PL spectroscopy measurements. The UV-vis spectra of these compounds in NMP solution are illustrated in Fig. 5a. The absorption spectra of **6** showed only one absorption band centred at 343 nm. The model compound **8** having two benzoyl units in the backbone exhibited two absorption bands: one intense at low energy between 260-310 nm, and the other located around 310-370 nm. The electronic properties of the polymers **9** depended on the electronic character and volumes of the substituent units present in the backbone.

Figure 5

In the absorption spectra of polymers **9** appeared two absorption bands more less evidentiated and blue shifted. This is due to a decrease of electron delocalization that occured in the case of the polymers. For polymers **9b** and **9c** containing hexafluoroisopropylidene and dimethylsilane bulky units, the absorption band from high energy was more intense comparatively with absorption characteristics of polymer **9a**. The peak at 330-343 nm could be attributed to the absorption of π electronic system delocalized along the 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4oxadiazole. The presence of electron donating dimethylamino group and aromatic ether linkage resulted in a higher absorption value due to π - π^* transition of oxadiazole group. Instead, the intense band at λ <300 nm resulted from transitions mainly centred on the phenyl groups introduced at

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backbone of compound **6**. The values of the maximum absorption bands of the studied compunds are shown in Table 2.

Table 2

The energy band gap (E_g) could be estimated from the following equation:

$$E_g = hc / \lambda_{edge} \tag{1}$$

where *h* is the Planck constant, *c* is the light velocity and λ_{edge} is the wavelength of the absorption edge. Table 2 shows the E_g values of the studied compounds. In NMP solution the E_g values were in the range of 3.11-3.16 eV and were not influnced to a great extent by the chemical structure.

Fig. 5b shows the emission spectra of the studied compound in dilute NMP solution. All the polymer solutions had emission maxima around 454 nm, under excitation wavelength λ_{ex} of 330 nm. At studied concentration (10⁻⁵M) the solutions showed one emission band, without other shoulders, as a consequence of the presence in their structure of only one kind of emission chromophore (2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole. The main photophysical properties (maximum emission wavelength, λ_{em} , full with at half maximum, fwhm, and Stokes shift) of the studied compounds are summarized in Table 3. The values of *fwhm* of the emision spectra were in the usual range (78-82 nm) and did not change significantly with the chemical structure. The Stokes shift is the difference between fluorescence and UV-vis absorption peaks. If the Stoke Shift is too small, the emittance and absorption spectra will overlap more and then the emitting light will be self-absorbed and the luminescent efficiency will decrease in the devices [36]. The polymers exhibited high Stokes shift values, in the range of 110-120 nm, indicating that self-absorption was reduced as a result of little overlap of the absorption and emitting spectra.

Table 3

The PL spectra of polymers **9** in solid state are shown in Fig. 6. The emission band was broad and structureless, having *fwhm* in the range of 109-164 nm. A blue shift of λ_{em} (by around 30 nm,

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Table 3) in the solid state can be observed when compared with λ_{em} in NMP solutions of the corresponding compounds. This blue shift can be explained as due to reduced rotational freedom of the polymer chains in the solid state. They tend to exhibit excimeric emissions due to the stacking of individual chromophores.

Figure 6

To obtain further information about the fluorescence properties the emission spectra were measured for polymer **9a**, at different excitation wavelengths (λ_{ex}), in DMAc. To investigate the change of fluorescence properties after excitation with different excitation wavelengths, the emission spectra were monitored using $\lambda_{ex} = 320$, 340, 360 and 380 nm (Fig. 7). Comparing these spectra the maximum of fluorescence intensity was obtained under excitation with 360 nm.

Figure 7

The fluorescence performance of the studied compounds (ability to emit light) was evaluated by their quantum yield values. The fluorescence quantum yield of **8** and **9** in dilute DMAc solution was measured using integrating sphere. The absolute values of fluorescence quantum yield reach 87.6% for **8**, 38.53% for **9a**, 52.76% for **9b** and 58.12% for **9c**, suggesting that these compounds exhibited high fluorescence. For studied compounds comparable emission characteristics (intensive blue emission, Stokes shifts values, high fluorescence quantum yield, full with at half maximum) with those of other polyamides with side oxadiazole rings [24, 37] were found.

In the color perception study, one of the first mathematically defined color spaces is the CIE-1931, XYZ color space [38]. The chromatic sensation of human eyes to a specific optical spectrum is usually characterized by a chromatic diagram. According to the available CIE standard, the chromaticity coordinates for **9a** solution in DMAc were x = 0.159 and y = 0.152. As shown in Fig. 8 they were located in the blue region, which means that this polymer emits pure blue light.

Figure 8

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Spectral properties before and after protonation with HCl were monitored in NMP solution. Fig. 9a presents UV-vis absorption spectra for unprotonated and protonated polymer 9a with HCl in NMP solution. It can be seen that by protonation the maximum absorption band from 335 nm was blue shifted. Thus, in the case of UV-vis absorption spectra of 9a in the presence of 0.5M and 2M HCl the maximum absorption band appeared around 317 nm. UV-vis spectrum of 9a-HCl (2M) showed an additional shoulder at 365 nm. The PL spectra of polymer **9a** in NMP solution, without and in presence of HCl, were presented in Fig. 9b. Protonation of the polymer determined a blue shift in the emission band in comparison with the unprotonated polymer solution (Table 4). It can be noticed that by increasing the HCl concentration a decrease of fluorescence intensity appeared. The fluorescence disappeared for a concentration of 2M HCl. As it can be seen from Table 4, the Stokes shift increased in the case of a concentration of 0.5 M HCl. The changes in the spectral properties (absorption and emission) after protonation can be attributed to the modification of the electronic structure of the polymer chains due to the interaction of oxadiazole rings and dimethylamino groups (nitrogen atom) with the proton of HCl. Namely, it is expected that the lone electron pair of nitrogen of 1,3,4-oxadiazole rings and dimethylamino groups to be protonated by a protic acid and the changes in optical properties to be induced [29,39].

Figure 9

Table 4

3.4. Fluorescence behavior of model compound 8 and polymer 9a in the presence of 3,5dinitrophenol

Studied compounds with above mentioned fluorescence characteristics (narrow and symmetric emission band, high quantum yield) attracted considerable attention for investigations of their interactions with some substances (e. g. nitroaromatic compounds) that would change their physical

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properties. Generally, the fluorescence intensity of fluorescent compounds decreases progressively with increasing concentrations of the nitroaromatic compounds. This intensity decrease of the emission (fluorescence quenching) occurs as a result of the molecular interactions that can lead to energy transfer, molecular rearrangement, ground-state complex and exciplex-formation, excited-state reactions etc [40,41]. In the fluorescence studies nitroaromatic derivatives can be used as active compounds, especially as fluorescence quenchers. The fluorescence quenching is a significant method of nitroaromatic compounds detection due to the sensitive and cost effective nature. The fluorescence quenching can take place by two different mechanisms, static and dynamic. Two studied compounds, **8** and **9a**, with high fluorescence signal, were chosen for investigation in the presence of 3,5-dinitrophenol (DNF).

The Stern-Volmer equation is usually used to investigate the fluorescence quenching process [39]:

$$I_0/I = I + K_{\rm SV}[Q] \tag{2}$$

where I_0 and I are the fluorescence intensities of the solute without and with quencher (DNF), respectively, K_{SV} is the Stern-Volmer (S-V) quenching constant and [Q] is the quencher concentration. The constant K_{SV} provides a direct measure of the quenching sensitivity.

Fig. 10a and 10b show the characteristic changes in excited state photophysical properties during the interaction of DNF with compound **8** and polymer **9a** in DMAc solution. On gradual addition of DNF, for both samples appreciable decreases in fluorescence intensity, without a shift in the emission wavelength, were observed indicating a strong excited state interaction of DNF with analysed samples. The Stern-Volmer plots I_0/I , at 454 nm, *versus* quencher concentration Q were linear at low concentrations (inset plots from Figs. 10a and 10b) but showed upward curvature at higher concentrations of the quencher. From the slopes of the initial linear parts of Stern-Volmer curves, the S-V constants were evaluated. It can be noticed that the samples **8** and **9a** exhibited closer K_{SV} values (1.54×10^{-3} and 1.79×10^{-3} molL⁻¹, respectively) indicating that the close quencher

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concentration was needed to quench the fluorescence. The upward curvature of the Stern-Volmer plot at higher concentrations suggested that the quenching process is not purely dynamic and may be due to a static contribution.

Figure 10

4. Conclusions

The incorporation of 2-(4-phenoxy)-5-(4-dimethylaminophenyl)-1,3,5-oxadiazole pendant segments into the macromolecular chain of polyamide or poly(amide-imide)s resulted in soluble polymers that retain a high thermal stability. The polymers can be processed into very thin films having the thickness in the range of tens of nanometres by using spin-coating technique. The films were smooth, homogeneous, practically without defects, when studied by atomic force microscopy. The poly(amide-imide)s can be processed from solution into thin flexible films having the thickness in the range of tens of micrometers by using casting technique. The polymers showed blue fluorescence in solution or in solid state. The presence of oxadiazole rings and dimethylamino groups containing nitrogen atoms available for interaction with Bronsted acids gave the opportunity for modification of polymer optical properties. Protonation with HCl as a dopant caused a significant decrease of fluorescence intensity. The Stern-Volmer equation used to investigate the fluorescence quenching process in the presence of DNF, showed that quenching process is not purely dynamic and may be due to a static contribution. All these properties, associated with an easy processability make the present polymers potential candidates for high-performance applications.

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Figure captations

Scheme 1. Preparation of diamine 6.

Scheme 2 Preparation of polymers 9.

Fig. 1. ¹H NMR (a), ¹³C NMR (b) and ¹H, ¹³C-HSQC NMR (c) spectra of **6** in DMSO- d_6 .

Fig. 2. ¹H NMR (a), ¹³C NMR (b) and ¹H, ¹³C-HSQC NMR (c) spectra of **9a** in DMSO-d₆.

Fig. 3. AFM images of **9a** on silicon wafer: 2D image (a), 3D image (b) and surface profile taken along the line in 2D image (c).

Fig. 4. TG (a) and DTG (b) curves of polymers 9.

Fig. 5. UV-vis absorption spectra (a) and PL spectra ($\lambda_{ex} = 330$ nm) (b) of **6**, **8** and **9**, in NMP

solution $(10^{-5} \mathrm{M})$.

Fig. 6. PL spectra of **9** (λ_{ex} = 330 nm) as films deposited on quartz slides.

Fig. 7. PL spectra of polymer **9a** in DMAc (10^{-5} M) at different λ_{ex} values.

Fig. 8. CIE chromaticity diagram calculated from emission spectra (excited at 330 nm) of polymer9a solution in DMAc.

Fig. 9. UV-vis absorption spectra (a) and PL spectra ($\lambda_{ex} = 340 \text{ nm}$) (b) for unprotonated and protonated polymer 9a with HCl in NMP solution.

Fig. 10. PL spectra of model compound 8 (a) and 9a (b) in DMAc ($\lambda_{ex} = 340$ nm), in absence and presence of increasing amounts of DNF. Inset shows the plot of I₀/I *versus* DNF concentration.

Table 1

The properties of polymers 9.

Polymer	$\eta_{\scriptscriptstyle inh}$	M_n	M_w	M_w/M_n	T_5	T_{10}	T_{max1}	T_{max2}	R
	$(dLg^{-1})^a$	$(g mol^{-1})$	$(g mol^{-1})$		$(^{\circ}C)^{b}$	$(^{\circ}C)^{c}$	$(^{\circ}C)^{d}$	$(^{\circ}C)^{e}$	$(\%)^{\mathrm{f}}$
9a	0.26	16100	20800	1.29	423	455	511	-	50.4
9b	0.53	32100	42300	1.40	433	473	538	609	53.7
9c	0.46	28600	41200	1.44	431	467	494	556	52.7

^a Inherent viscosity.
^b Temperature of 5% weight loss.
^c Temperature of 10% weight loss.
^d First maximum polymer decomposition temperature.
^e Second maximum polymer decomposition temperature.
^f Char yield at 700 °C.

Sample	$\lambda_{max1} (nm)^{a}$	$\lambda_{max2} (nm)^{b}$	$\lambda_{edge} (\mathrm{nm})^{\mathrm{c}}$	$E_g (eV)^d$
6	-	343	398	3.11
8	278	343	396	3.13
9a	279	334	393	3.15
9b	276	336	392	3.16
<u>9c</u>	275	334	394	3.14

Table 2

Optical properties of **6**, **8** and **9** in NMP solution (10^{-5} M) .

^a wavelength of the first maximum absorption band. ^b wavelength of the second maximum absorption band. ^c wavelength of the absorption edge. ^d the energy band gap.

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Sample	NMP so	Solution $(10^{-5} \mathrm{M})$ (2)	Solid state ($\lambda_{ex} = 330 \text{ nm}$)			
	λ_{em} (nm) ^a Stokes shift		Fwhm (nm) ^b	$\lambda_{em} (nm)^a$	Fwhm (nm) ^b	
		(nm)				
6	453	110	78	-	-	
8	456	113	81	-		
9a	453	119	80	422	164	
9b	454	118	81	423	114	
9c	454	120	82	422	109	
^a Maximum emin ^b Full with at hal	ssion wavel f maximum	ength.				

Table 3.Fluorescence properties of 6, 8 and 9 in NMP solution and in solid state.

<u>340 nm).</u>				
Sample	$\lambda_{abs} (nm)^{a}$	$\lambda_{em} (\mathrm{nm})^{\mathrm{b}}$	Fluorescence intensity	Stokes shift
			at $\lambda_{em}(a.u.)$	(nm)
9a	335	453	300	122
9a-0.01 M HCl	-	455	275	-
9a- 0.1 M HCl	-	452	272	-
9a- 0.5 M HCl	317	459	82.8	137
9a- 1 M HCl	-	437	61.91	- `
9a- 2 M HCl	317, 365	424	5.68	-

Table 4.

The optical properties for unprotonated and protonated polymer 9a with HCl in NMP solution (λ_{ex} = 340

^a Wavelength of the maximum absorption band. ^b Maximum emission wavelength.

Scheme 1



Scheme 2









Figure 2









Figure 3









Figure 6



Figure 7















Graphical Abstract



