



*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 65th anniversary*

STUDY OF FLUORINATED POLYIMIDES CONTAINING FUSED AROMATIC RINGS

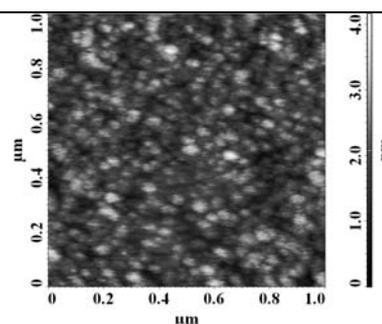
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This article presents the synthesis and study of the properties of fluorinated polyimides containing fused aromatic rings such as naphthalene or perylene. The fluorinated groups which are trifluoromethyl substituents on benzene rings were meant to enhance the solubility and to lower the glass transition temperature, hence to improve the processing of these polymers into thin films and coatings. The light emitting ability of these polyimides was evaluated on the basis of photoluminescence spectra which were recorded for polymer solutions and thin films.



INTRODUCTION

Aromatic polyimides containing five-member imide rings exhibit excellent thermal and thermooxidative stability, and outstanding mechanical and electrical properties which make them very attractive for a variety of high performance applications.¹⁻⁴ Polyimides containing six-member imide rings with naphthalimide or perylene imide structures, although showing high thermal resistance and very good hydrolytic stability, have received little attention primarily due to the inability of obtaining soluble precursors for fabrication. Previous investigations have shown that polynaphthylimides, which are formed when either naphthalene-tetracarboxylic acid dianhydride or bis(naphthalic anhydrides) are employed as monomers, display superior chemical, thermal and

fire resistance, compared with the analogous systems derived from bis(phthalic anhydrides).⁵⁻⁸ More recently, naphthalene and perylene units have been introduced into the main chain of π -conjugated polymers such as polyphenylenevinylene, polyfluorene, polythiophene, polyoxadiazole, polycarbazole with the aim to develop new emissive materials for use in organic light-emitting diodes.⁹⁻¹² But, the majority of polyheteroarylenes based on naphthalic dianhydrides or on perylene dianhydride are difficult to process, being infusible and insoluble in common organic solvents and soluble only in strong acids. Being known that the introduction of flexible groups or voluminous units in the backbone of aromatic polymers can lead to soluble products, a combined approach was undertaken through the synthesis of six-member polyimides containing flexible groups such as

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hexafluoroisopropylidene, siloxane, diphenylsilyl, and other.¹³⁻¹⁸ In our continuous efforts to obtain aromatic polymers with improved solubility and processing capability, we found it interesting to synthesize six-membered polyimides containing trifluoromethyl substituents, so that the resulting polymers would maintain the high thermal and thermooxidative stability while being easy processable. Therefore, here we present a series of fluorinated polyimides containing fused aromatic rings, such as naphthalene or perylene, and trifluoromethyl units and the study of their properties, particularly solubility, thermal stability, photo-optical properties, and film forming ability.

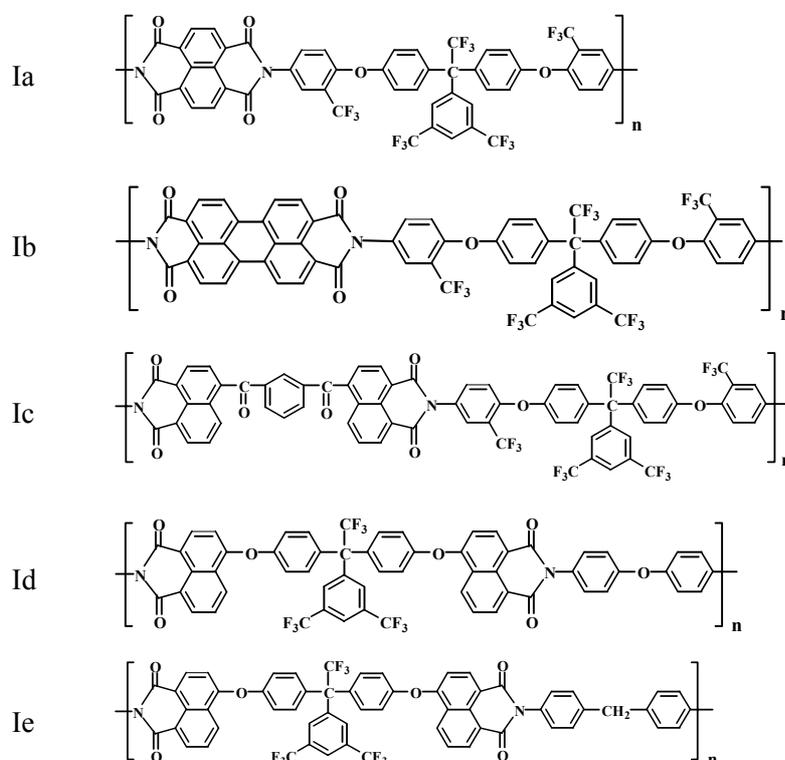
RESULTS AND DISCUSSION

The fluorinated polyimides containing fused aromatic rings (I) are based on the polycondensation reaction of aromatic dianhydrides having fused aromatic rings, such as 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride, 3,4,9,10-perylene-tetracarboxylic acid dianhydride,^{19,20} 1,3-bis(carbonyl-naphthalene)-phenylene tetracarboxylic acid dianhydride^{5,18} and 1-[3',5'-trifluoromethyl-phenyl]-1,1-bis(4'-phenoxy -naphthalene)]-2,2,2-trifluoroethane tetracarboxylic acid dianhydride,^{21,22} with aromatic diamines, such as 4,4'-

diaminodiphenylether, 4,4'-diaminodiphenylmethane and a diamine having trifluoromethyl substituents, namely 1,1-bis[4-(4'-amino-2'-trifluoromethylphenoxy) phenyl]-1-[3'',5''-bis(trifluoromethyl)-phenyl]-2,2,2-trifluoro-ethane.²² The structures of polymers are shown in Scheme 1.

All these polymers containing trifluoromethyl groups are soluble in N-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and phenolic solvents. The good solubility makes the present polymers potential candidates for practical applications in solution-processing techniques. Reduced viscosity values (in NMP at 25°C) of these polymers are in the range of 0.20–0.84 dL/g.

Thermogravimetric analysis evidenced a high thermal stability of all these polymers, their decomposition temperature being in the range of 490–500°C, as determined from the onset of the TGA diagram. Except for polyperyleneimide Ib which did not show a T_g until the onset of degradation (500°C), all the other polymers did exhibit glass transition, in the temperatures range of 270–290°C, determined by DSC method, being quite high but still with a large interval between glass transition and decomposition which could facilitate the processing of these polymers by a thermoforming technique.



Scheme 1 – Structures of fluorinated polyimides containing fused aromatic rings (I).

Solutions of these polymers in N-methylpyrrolidone were processed into thin films having the thickness in the micrometer range and into very thin films having the thickness in the nanometer range by drop-casting technique onto silicon wafers. The quality and morphology of very thin films were studied by atomic force microscopy (AFM). The films made from polyimides Ia and Ib were smooth and homogeneous, without cracks or pinholes, and were self-organized into vertically segregated structures. The average roughness of a surface area of $1\ \mu\text{m} \times 1\ \mu\text{m}$ was 0.51 nm for Ia and 2.15 nm for Ib. Typical AFM images are shown in Fig. 1. The films of polymer Id exhibited a homogeneous surface, without pinholes or cracks, as well, and with root mean square roughness (RMS) in the range of 3-5 Å, being of the same order of magnitude as that of highly polished silicon wafers which were used as substrates. It means that the present films are very smooth, practically defectless. All the films had strong adhesion to silicon wafers.

There is currently much interest in high-brightness light-emitting diodes (LEDs) for use in full color displays, full color indicators and light sources for lamps, with characteristics of high efficiency and high reliability. Among the three primary colours, green and red LEDs have been successfully fabricated with high efficiency, while the performance of blue devices still needs to be improved. Because blue-light emissions are associated with higher energy gaps, higher electric field intensities have to be applied to the light-emitting layer. Consequently higher thermal and oxidative stabilities are demanded for the blue light-emitting polymers. The use of electroluminescent thin films made from highly thermostable polymers would avoid the thermal degradation in the final device while in service at

elevated temperatures. In addition blue light can be converted to green or red by using proper dyes, which means that a blue light-emitting device alone is capable of generating all colors, while green or red cannot emit blue light by this method. Since naphthylimide and perylenediimide units are known as light-emissive,^{17,23} the light-emitting properties of the present polyimides have been investigated. The light emitting ability of polymers Ia, Ib and Id was evaluated on the basis of photoluminescence (PL) spectra which were recorded for polymer solutions in 1-methyl-2-pyrrolidinone (NMP) and thin films drop-cast from NMP solution, after irradiation with UV light of different wavelengths. The dominant aspect in these materials is their extended conjugated π -system; such extension is reflected by the electronic absorption spectrum. The absorption spectra of polymer solutions in NMP and of the films cast from such solutions are presented in Fig. 2.

It was found that the polyimide Ia containing naphthylidimide chromophore showed two strong UV absorption maxima at 360 and 380 nm and one shoulder at 342 nm, while polyimide Id containing naphthylimide chromophore presents one strong UV absorption maxima at 358 nm and two shoulders at 342 and 377 nm (Table 1). These absorption maxima are mainly determined by the chain segments containing naphthylidimide or naphthylimide chromophores of different conjugation lengths. The polymer containing perylenediimide unit "Ib" showed two strong peaks at 492 and 521 nm due to the absorption of this chromophore and one weak and large peak centred at 375 nm (Fig. 2) being attributed to spin-allowed π - π^* transitions involving the imide-phenyl framework.

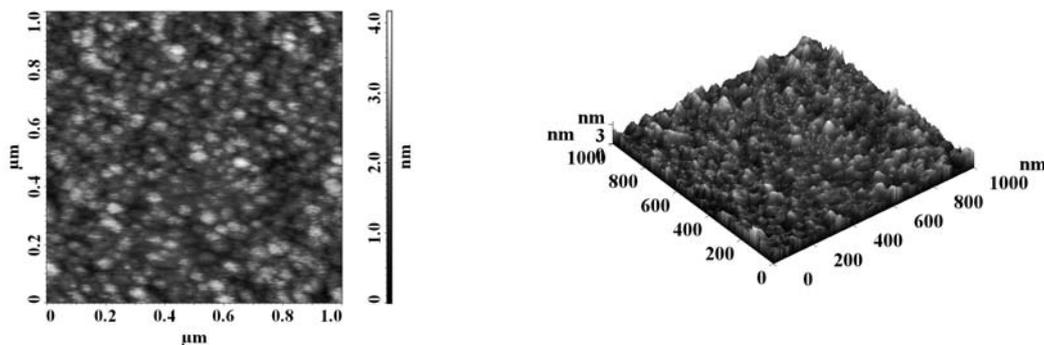


Fig. 1 – AFM images of a film made from polyimide Ia, as-deposited on silicon wafer.

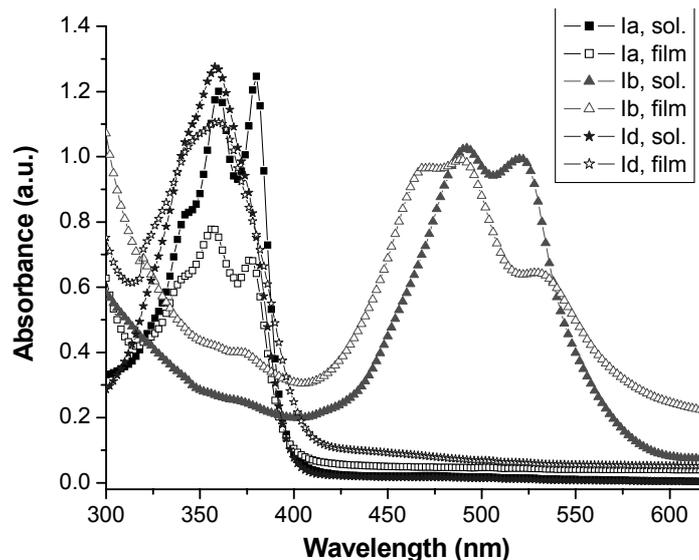


Fig. 2 – UV absorption spectra of polymers Ia, Ib and Id.

Table 1

Optical properties of polyimides containing fused aromatic rings in solution and in film state

Polymer	UV, sol	UV, sol	UV, film	UV, film	$E_{g,sol}$ (eV)	$E_{g,film}$ (eV)
	λ_{abs} , nm	λ_{edge} , nm	λ_{abs} , nm	λ_{edge} , nm		
Ia	342 ^s , 360, 380	397	339 ^s , 357, 377	401	3.13	3.10
Ib	375 ^w , 492, 521	592	373 ^w , 468, 490, 533	611	2.10	2.03
Id	342 ^s , 358, 377 ^s	402	346 ^s , 361	416	3.09	2.98

λ_{abs} – wavelength of the maximum absorption peak; λ_{edge} – wavelength of the absorption edges of the optical absorption spectra; E_g – energy band gap calculated from the UV absorption spectra; s – shoulder; w – weak

In thin films cast from NMP solutions the absorption maxima of polyimide Ia are blue-shifted by 3 nm with respect to the absorption of the isolated molecules, whereas in the case of polyimide Id they are red-shifted with 2-3 nm. These small shifts of the UV maximum in solid state as compared with solution could account for negligible intermolecular interactions of the conjugated naphthylimide segments of the polymer chains. For polymer Ib a significant blue-shift was noticed of the maximum from the highest wavelengths in film state as compared with solution. Interestingly, while most conjugated polymers exhibit bathochromic shifts from solution to solid state, the absorption spectra of these polymers exhibit hypsochromic shifts in thin films, which is indicative of a solid-state organization of perylenediimide chromophores through aggregation. Usually, the blue shifts in photochemistry are associated with the formation of H-aggregates. The self-association of dyes in solution or at the solid-liquid interface is a

frequently encountered phenomenon in dye chemistry owing to strong intermolecular Van der Waals-like attractive forces between the molecules. The hypsochromically shifted H-bands of the aggregates have been explained in terms of molecular exciton coupling theory, *i.e.*, coupling of transition moments of the constituent dye molecules. The dye molecules aggregate in one dimensional assembly in a parallel way (plane to plane stacking) to form a ladder-type arrangement.^{24, 25}

The absorption edge, being a long-wavelength wing of the longest-wavelength band of the spectrum, moves to longer wavelength (smaller energy) for polymer film when compared with solution of the same polymer. It means that conformation of polymer chain can be different depending on the surroundings.²⁶

The energy band gap (E_g) can be estimated from the following equation: $E_g = h \times c / \lambda_{edge}$, where h is the Planck constant, c is the light velocity, and λ_{edge} is the wavelength of the

absorption edges of the optical absorption spectra. This method allows estimating and comparing the energy gaps for polymers in the form of solution and thin film, as shown in Table 1. The energy gap of the polyimides under study varies from 2.10 eV to 3.13 eV for solutions and from 2.03 eV to 3.10 eV for films. The highest energy bandgap was found for polymers containing naphthyldiimide chromophore and the smallest energy bandgap was found for polymer having perylenediimide chromophore. The E_g values of the films are smaller than the E_g values of the corresponding solutions, due to the more aggregated conformation of polymer main chains in solid state.

Since the absorption spectra present multiple absorption peaks for each individual chromophore, and even for conjugated parts containing these chromophores we investigated the photoluminescence (PL) ability of these polymers by exciting with UV or visible light of different wavelengths. Maximum emission wavelengths values of the polyimides containing fused ring in solution and solid state are given in Table 1.

By exciting at 360 nm, polymers Ia and Id in solution displayed the main emission maxima in the blue domain at 468 and 432 nm, respectively, due to the emission of naphthyldiimide and naphthylimide chromophores. Some additional shoulders at 414, 427 and 442 nm were registered only for Ia by excitation at this wavelength that could be attributed to the PL emission from naphthylimide excimers. A weak red shift of the main PL maximum of Ia was registered when the excitation was done with 380 nm, whereas no shift took place for Id when the excitation was made with 340 nm. The emission spectra of polyperyleneimide Ib in NMP solution excited by a 490 nm or 520 nm light showed two peaks in the green-yellow spectral range, at 537 and 578 nm, corresponding to the emission of perylenediimide moieties (Table 2). Fig. 3 shows the photoluminescence spectra of these polyimides in solution by excitation with light of different wavelengths.

Table 2

Fluorescence properties of polyimides (λ_{PL} =wavelength of maximum PL emission peak; s= shoulder)

Polymer	Solution		Film	
	λ_{PL} (nm)	Stokes shift (nm)	λ_{PL} (nm)	Stokes shift (nm)
Ia (ex. 360 nm)	414 ^s , 442 ^s , 468, 527 ^s	108	414, 480 ^s , 528 ^s	37
Ib (ex. 549 nm)	537, 578	16	-	-
Id (ex. 340 nm)	432	74	414, 481 ^s , 520 ^s	53

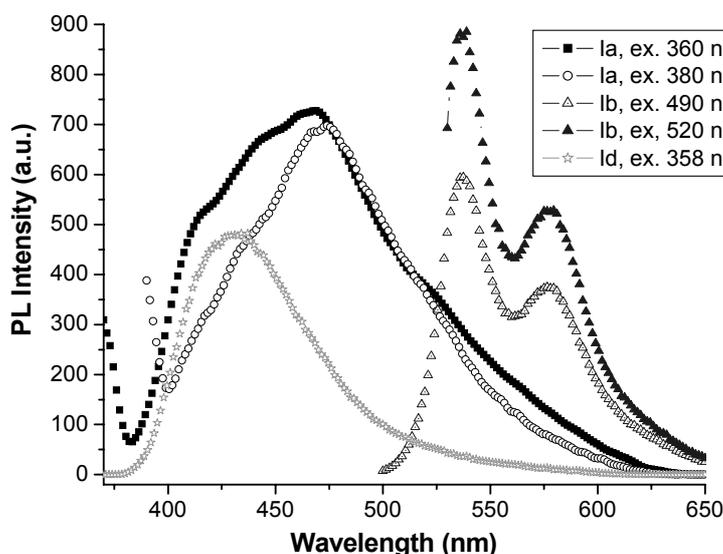


Fig. 3 – PL spectra of polyimides Ia, Ib and Id in solution by excitation with light of different wavelengths.

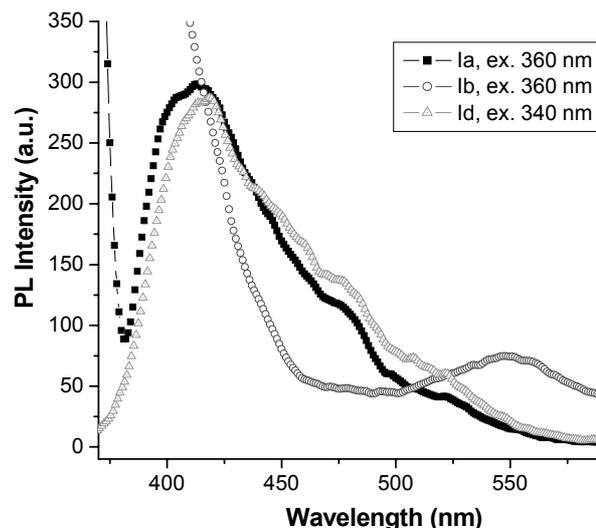


Fig. 4 – Photoluminescence (PL) spectra of polyimide films Ia, Ib and Id.

The PL spectra of films cast from polymer Ia and Id solutions showed one maximum in the range of 414-418 nm and two shoulders in the range of 441-442 nm and 520-528 nm (Table 2). A significant blue-shift of the main PL maximum in film (414 and 418 nm) compared with solution (468 and 432) of these polymers was noticed. It could account for intermolecular interactions of the conjugated parts of the polymer chains and some degree of H-aggregates formation, being an indicative of a solid-state organization of these polymers in solid state. The weak, shoulders-like emissions being present in the PL spectra of both polyimide films are due to the various degrees of aggregation and the excimer formation in the films, leading to photoluminescence quenching, emission band broadening, and bathochromic shift.²⁷ The photoluminescent behavior of polyimide Ib changed significantly from solution to solid state. The light-emitting ability of this polymer was observed only by exciting at 370 nm. The PL spectra of this polymer presented one weak PL peak in the green domain at 550 nm due to the emission of perylenediimide moieties. When the excitation was done with higher wavelengths no emission attributed to this chromophore was observed. This behavior can be ascribed to the high content of perylenediimide chromophore/structural unit which leads to fluorescence quenching through aggregation. Fig. 4 shows some PL spectra of these polymers in solid state.

The Stokes shift (the difference between the main fluorescence and UV-vis peaks) of polymers Ia, Ib and Id in solution and solid state are of 16-108 nm (Table 2). Therefore, all these

polyimides display enough high values of the Stokes shift for good luminescence efficiency.

EXPERIMENTAL

3.1. Synthesis of polymers

Fluorinated polyimides containing fused aromatic rings (I) were prepared by solution polycondensation reaction of equimolar amounts of an aromatic dianhydride containing fused aromatic rings such as 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride, 3,4,9,10-perylene-tetracarboxylic acid dianhydride,^{19,20} 1,3-bis(carbonyl-naphthalene)-phenylene tetracarboxylic acid dianhydride^{5,18} and 1-[3',5'-trifluoromethyl-phenyl]-1,1-bis(4'-phenoxy-naphthalene)]-2,2,2-trifluoroethane tetracarboxylic acid dianhydride,^{21, 22} with an aromatic diamine such as 4,4'-diaminodiphenylether, 4,4'-diaminodiphenyl-methane and a diamine containing trifluoromethyl substituents, namely 1,1-bis[4-(4'-amino-2'-trifluoromethylphenoxy) phenyl]-1-[3',5'-bis(trifluoromethyl)-phenyl]-2,2,2-trifluoro-ethane.²² The reaction was performed under conditions of high temperature catalytic polycondensation in phenol as solvent. A mixture of benzoic acid and benzimidazole was used as catalyst, and the synthesis was accomplished under homogeneous conditions at 80–180°C for 15-20 h in argon. The fluorinated polyperyleneimide Ib was prepared in chlorophenol medium at 210°C for 10 h.

3.2. Measurements

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) by using MOM-type Derivatograph made in Budapest, Hungary, operating in air at a heating rate of 12°C/min. The glass transition temperature (T_g) was measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of 20°C/min. The mid-point of the inflection curve resulting from the typical second heating cycle was considered as T_g of polymers. The morphology of very thin films as-deposited on silicon wafers was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscope Solver PRO-M, NT-MDT made in Russia, in semi-contact mode. The UV-Vis absorption and photoluminescence spectra of the polymers were registered

with Specord M42 apparatus and Perkin Elmer LS 55 apparatus, respectively, by using very diluted polymer solutions with concentration of about 10^{-5} M and very thin films having the thickness in nanometer range.

CONCLUSIONS

Fluorinated polyimides containing aromatic fused rings were obtained by polycondensation reaction of different aromatic diamines, some of them containing trifluoromethyl groups, with naphthalene- or perylene-containing dianhydrides. All the polymers containing trifluoromethyl groups were soluble in polar amidic and phenolic solvents. Very thin films having the thickness in the nanometer range were prepared from polymer solutions. These films were smooth and homogeneous, without cracks or pinholes, some of them being self-organized into vertically segregated structures, whereas others showed a neat surface. These six-member polyimides are highly thermostable, their initial decomposition temperature being above 490°C. The T_g value is high enough (270–290°C), but still with a large window between T_g and decomposition temperature which may be useful for their processing by thermoforming techniques. These polyimides presented absorption peaks characteristic for naphthylidimide chromophore at 360 and 380 nm, for naphthylimide chromophore at 358 nm and for perylenediimide chromophore at 492 and 521 nm. Excited with UV light, the solutions of polymers containing naphthylidimide or naphthylimide chromophores displayed the main PL maxima in the blue domain due to the fluorescence emission of these chromophores, while the polyperyleneimide in NMP solution excited by 490 nm or 520 nm light showed two peaks in the green-yellow spectral range corresponding to the emission of this chromophore. A significant blue-shift of the main PL maximum in film compared with solution was noticed for those polymers containing naphthalene, being an indicative of a solid-state organization of these polymers in solid state. No emission was observed in solid state for peryleneimide-containing polymer. The high-performance properties of these polymers recommend them for use to fabricate electroluminescent devices with high thermal stability.

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