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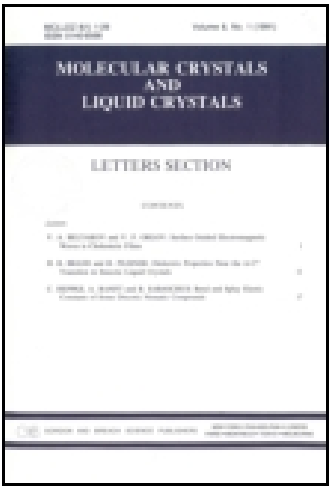

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Hole-Transporting Pyrenyl-Substituted Derivatives of Fluorene and Carbazole

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Published online: 28 Mar 2014.

To cite this article: A. Tomkeviciene, J. V. Grazulevicius & V. Jankauskas (2014) Hole-Transporting Pyrenyl-Substituted Derivatives of Fluorene and Carbazole, Molecular Crystals and Liquid Crystals, 590:1, 29-34, DOI: 10.1080/15421406.2013.873637

To link to this article: http://dx.doi.org/10.1080/15421406.2013.873637

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Mol. Cryst. Liq. Cryst., Vol. 590: pp. 29–34, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.873637

Hole-Transporting Pyrenyl-Substituted Derivatives of Fluorene and Carbazole

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The properties of the pyrenyl-substituted fluorene and carbazole compounds exhibiting charge carrier transport properties are reported. Cyclovoltammetric experiments revealed the electrochemical stability of the fluorene compounds. In contrast to the fluorene derivatives, the carbazole compounds showed nonreversible oxidations in the CV experiments. The pyrene-substituted fluorene and carbazole derivatives showed capability of transporting holes as characterized by xerographic time of flight technique. Ionization potential values measured by electron photoemission spectroscopy were found to be in the range of 5.70 eV – 5.93 eV.

Keywords Carbazole; Fluorene; Ionization energy; Charge mobility

Introduction

Charge-transporting materials are known for their widespread use in diverse electronic and optoelectronic applications [1]. Among the most exploited aromatic units are carbazole and fluorene, which, in fact, by proper substitution are capable of delivering multifunctional properties. Functionalization of carbazole and fluorene units via substitution at 2,7-positions demonstrated great potential and advantage (over typical 3,6-substitution for the carbazole moiety) for light-emitting device applications by yielding extended conjugation, enhanced emission efficiency and, in some cases, bipolar charge carrier transport with electron and hole mobilities as high as 10^{-3} cm^2/V·s [2].

In our previous study [3], fluorene and carbazole derivatives substituted with pyrene at 2- and 2,7-positions investigated as promising blue light emitters. In this paper, we report on the electrochemical and photoelectrical properties of pyrenyl-substituted fluorene and carbazole compounds with potential application in organic optoelectronics. Pyrene derivatives were only recently started to be used as organic semiconductors for advanced applications in materials science and organic electronics in particular [4].

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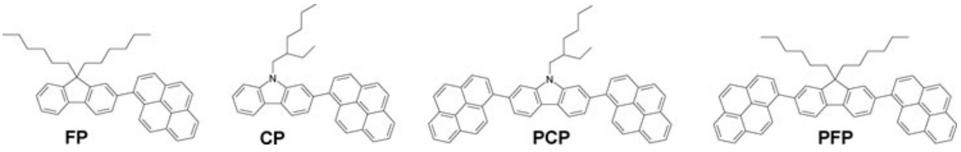

Scheme 1. Molecular structures of studied materials.

Experimental

Materials

2-Pyrenyl-9,9-dihexylfluorene (FP), 2-pyrenyl-9-(2-ethylhexyl)carbazole (CP), and 2,7-dipyrenyl-9-(2-ethylhexyl)carbazole (PCP) were synthesized by a Suzuki coupling reaction as described in literaure [3]. 2,7-Dipyrenyl-9,9-dihexylfluorene (PFP) was prepared by the reported procedure [5].

Instrumentation

Cyclic voltammetry (CV) measurements were carried out by a three-electrode assembly cell from Bio-Logic SAS and a micro-AUTOLAB Type III potentiostat-galvanostat. The working electrode was a glassy carbon of 0.12 cm^2 surface although the reference electrode and the counter electrode were Ag/Ag^+ 0.01 M and Pt wire respectively. Argon-purged dichloromethane (Fluka) with tetrabulthylammonium perchlorate (TBAP; Aldrich) 0.1M as electrolyte containing 10^{-3} $mol{\cdot}L^{-1}$ of electroactive compunds were used for the studies. The ionization energy (E_I) of the layers of the compounds was measured by the electron photoemission in air method as described earlier [6]. The measurement error was evaluated as 0.03 eV. The samples for the measurements were prepared by dissolving materials in THF and by coating on Al plates pre-coated with $\sim$0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The measurement method is, in principle, similar to that described in literature [7]. Hole drift mobility was measured by xerographic time of flight technique (XTOF) [8,9]. The samples for the measurement were prepared by drop casting of the solutions of compounds in tetrahydrofuran onto a polyester film with Al layer [10].

Results and Discussion

The structures of pyrenyl-substituted fluorene and carbazole derivatives FP, CP, PFP and PCP are illustrated in Scheme 1.

The synthesis of the compounds has already been described in the literature [3]. These compounds exhibited high fluorescence quantum efficiency in both dilute solutions (up to 80%) and solid matrix (up to 70%), short fluorescence lifetimes (1-2 ns), what resulted in relatively low threshold of amplified spontaneous emission [3].

Electrochemical properties

The electrochemical properties of the compounds were studied by CV. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as electrolyte, $Ag/AgNO_3$ as the reference

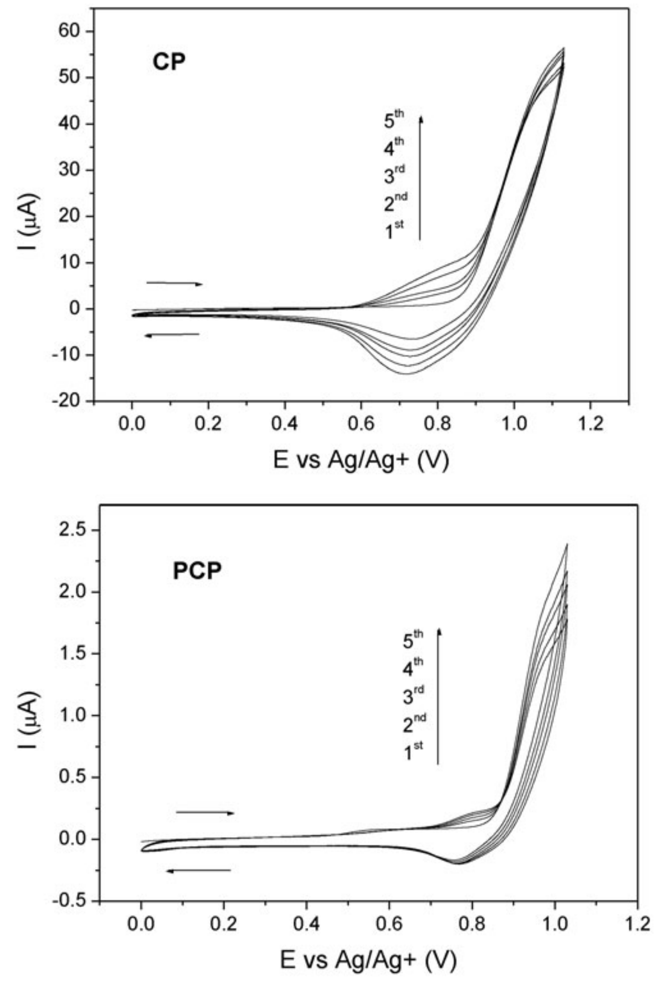

Figure 1. Cyclic voltammograms of CP and PCP recorded at scan rate of 50 mVs^{-1} vs Ag/Ag+ in a solution of TBAP (0.1 M) in CH_2Cl_2.

electrode and a Pt wire counter electrode. The experiments were calibrated with the standart ferrocene/ferrocenium redom system [11].

The CV curves of pyrenyl-substituted carbazole derivatives CP and CPC are shown in Figure 1. In the first redox cycle the oxidation of CP and CPC started at 0.87 V and 0.86 V, respectively (Table 1). As the CV scans continued, compounds CP and CPC exhibited two

Table 1. Electrochemical characteristics and E_I values of FP, CP, PFP and PCP

Compound	FP	CP	PFP	PCP
E_{onset} (V)	0.93	0.87	0.92	0.86
E_I [a] (eV)	5.93	5.77	5.87	5.70

[a] Ionization energy was measured by the photoemission in air method from films.

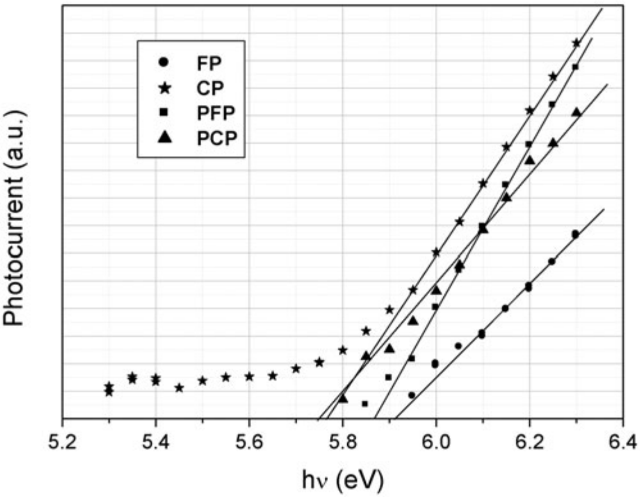

Figure 2. Electron photoemission spectra of the amorphous films of FP, CP, PFP and PCP recorded in air at 25°C.

oxidation peaks in the region of 0.80 – 1.12 V, one of which was absent in the first cycle. It seems that the carbazole moieties were oxidized in the first scan, followed by irreversible formation of new carbazolyl compound [12]. The oxidation and reduction potentials of CP and CPC gradually shifted to positive and negative fields as the scans continued. This observation can be explained by the formation of films on the working electrode surface. The film thickness gradually increased upon CV scanning.

In contrast to the pyrenyl-substituted carbazole derivatives, the fluorene-based compounds FP and PFP were found to be electrochemically stable. Apparently the C-3- and C-6 positions of fluorene rings are not activated after introduction of the substituents into C-2 and C-7 positions. The oxidation of the fluorene compounds FP and PFP started at 0.93 V and 0.92 V in the first cycle, which was somewhat higher than the corresponding values of carbazole compounds CP (0.87 V) and CPC (0.86 V) (Table 1). Repeated oxidation and reduction cycles did not change the redox potentials of the fluorene compounds FP and PFP.

Photoelectrical properties

Considering the application of organic semiconductors in optoelectronic devices the important characteristic is solid state ionization energy (E_I). The ionization energies of the solid layers of FP, CP, PFP and PCP were measured by the electron photoemission in air method. The results are presented in Table 1. Usually the photoemission experiments are carried out in vacuum, and high vacuum is one of the main requirements for these measurements. If the vacuum is not high enough, the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated were stable enough to oxygen and the measurements could be carried out in air. Electron photoemission spectra of the amorphous films of the compounds are presented in Figure 2. The values of E_I of the pyrenyl-substituted carbazole derivatives CP and PCP were found to be lower than those of the fluorene-based compounds FP and PFP. E_I values are not strongly effected by the number of pyrenyl groups.

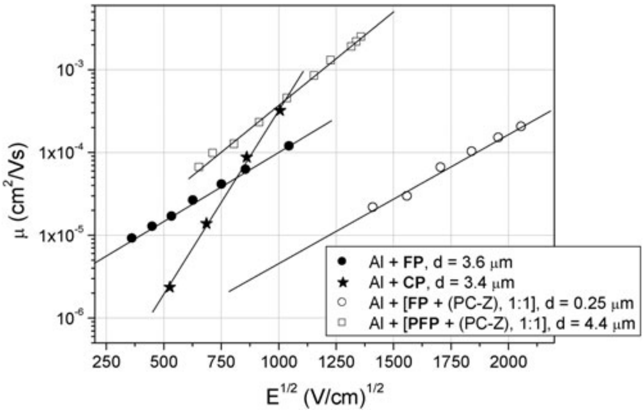

Figure 3. Electric field dependencies of the hole drift mobility in charge transport layers of compounds FP, CP and of compounds FP, PFP doped in PC-Z (50%).

The xerographic time-of-flight measurements were used to characterize charge-transporting properties of pyrenyl-substituted fluorene and carbazole compounds. Figure 3 shows electric field dependencies of hole drift mobilities (μ) in the amorphous layers of compounds FP, CP and in the films of bisphenol Z polycarbonate molecularly doped with compounds FP and PFP. The linear dependencies of the hole drift mobility on the square root of the electric field E are observed. Zero field mobilities (μ_o) and mobilities (μ) observed at the electric field of 6.4×10^5 V cm^{-1} are given in Table 2. The disubstituted PFP and PCP compounds are crystalline materials [3] and it was impossible to obtain morphologically stable amorphous layers of these compounds for the hole drift mobility measurements.

The highest hole mobility, exceeding 10^{-3} cm^2 V^{-1} s^{-1}, was observed in amorphous film of the solid solution of pyrenyl disubstituted fluorene compound PFP in bisphenol Z polycarbonate (PC-Z). This is relatively high charge mobility for molecularly doped polymer. Hole drft mobility of the order 10^{-2} cm^2 V^{-1} s^{-1} can be predicted for the amorphous film of the pure compound [13]. The comparison of charge mobility data for the amorphous film of pure FP with that of its molecular mixture with PC-Z, shows that mobility value for FP is more than by one order of magnitude higher than that observed for the molecular mixture with PC-Z.

Table 2. Hole mobility data of the pyrenyl-substituted derivatives of fluorene and carbazole

Transport material, host polymer	d [a], (μm)	μ_o [b], (cm^2 V^{-1} s^{-1})	μ [c], (cm^2 V^{-1} s^{-1})
FP	3.6	2.3×10^{-6}	4.8×10^{-5}
CP	3.4	1.0×10^{-8}	4.0×10^{-5}
FP + (PC-Z), 1:1	0.25	—	2.2×10^{-6}
PFP + (PC-Z), 1:1	4.4	2.0×10^{-6}	1.3×10^{-4}

[a] Layer thickness; [b] The zero field hole drift mobility; [c] The hole drift mobility at an electric field of 6.4 Í 10^5 V cm^{-1}.

Conclusions

The pyrenyl-substituted fluorene and carbazole derivatives were investigated as potential charge transporting materials. The electrochemical and photoelectrical properties were studied. In electrochemical measurements the pyrenyl-substituted carbazole and fluorene compounds behaved differently. Fluorene-based compounds were found to be electrochemically stable, while the oxidation of the carbazole compounds was irreversible. The ionization energies of mono- and disubstituted fluorene and carbazole compounds ranged from 5.70 to 5.93 eV, as established by electron photoemission spectrometry. Pyrenyl-substituted carbazole derivatives showed lower ionization energies than the analogous fluorene derivatives. Hole mobility, exceeding 10^{-3} cm^2 V^{-1} s^{-1}, was observed in amorphous film of the solid solution of pyrenyl disubstituted fluorene compound in bisphenol Z polycarbonate.

Acknowledgments

This research was funded by the European Social Fund under the Global Grant measure. We thank habil. dr. V. Gaidelis for the help in ionization potential measurements.

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