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Crosslinkable Fluorene-Based Derivatives as Materials for Light Emitting Diodes

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A series of cross-linkable fluorene-based derivatives have been synthesized by the multistep synthetic rout. Characterization of their structure by ¹H NMR and mass spectrometry is presented. The synthesized materials were examined by various techniques including differential scanning calorimetry, thermogravimetry, UV, fluorescence and electron photoemission spectrometries. It is established that the new derivatives have large triplet energies and could be used as host materials in phosphorescent light emitting diodes. The device fabricated with the use of one of the new hosts reached a brightness of 1700 cd/m² and a current efficiency of 3.4 cd/A.

Keywords: aromatic amine; cross-linkable material; ionization potential; light emitting diode; triplet energy

1. INTRODUCTION

Improvements in the performance of organic light emitting diodes (OLEDs) over the past decade have resulted in commercially available products. Organometallic small molecule phosphor-doped devices have demonstrated by far the highest efficiency [1,2]. In phosphorescent devices, to reduce the quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet-triplet

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annihilation, etc., triplet emitters of heavy-metal complexes are normally used as emitting guests in a host material, and thus suitable host materials are of equal importance for phosphorescent OLEDs. For the electrophosphorescence from triplet guests, it is essential that the triplet level of a host be larger than that of the triplet emitter to prevent the reverse energy transfer from the guest back to the host and to effectively confine triplet excitons on guest molecules [3,4].

We have observed earlier that carbazole- and diphenylamine-based derivatives demonstrate good hole transport properties and large triplet energies [5,6]. Here, we report the molecular design of materials containing the non-conjugated linking of fluorene with carbazol-9-yl or diphenylamino fragments. The substituted fluorenes demonstrate rather large triplet energies and are potential host materials for green or red electro-phosphorescent devices. On the other hand, the derivatives contain cross-linkable oxetanyl groups and could be used for the preparation of a insoluble host-guest system which is suitable for the preparation of multilayer OLEDs by spin-coating [7].

2. EXPERIMENTAL

2.1. Instrumentation

^1H NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using a Perkin Elmer FT-IR System. UV spectra were measured with a Spectronic GenesysTM 8 spectrometer. Fluorescence (FL) spectra were recorded with a MPF-4 spectrometer. Differential scanning calorimetry (DSC) measurements were carried out using a Bruker Reflex II thermosystem. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10°C/min.

The ionization potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air which was described earlier [8]. The measurement method was, in principle, similar to that described by Miyamoto *et al.* [9].

The electro-phosphorescent devices were fabricated on glass substrates and had the typical structure with the organic layers sandwiched between a bottom ITO anode and a top metal cathode (Ca/Al). Before use, the ITO-coated glass substrates were carefully cleaned and treated with UV/ozone right before the deposition of organic layers. PEDOT layers were deposited by spin-coating and heated at 120°C for 30 min. The electro-phosphorescent layers were

made by spin-coating: e.g., a ~100-nm layer of the host (mixture-7:3 of **3** or **6** with PBD) containing 2 wt.% of guest {Ir(ppy)₃} onto the substrates with PEDOT. Evaporation of the cathode was done in a vacuum evaporation equipment.

The current–voltage and luminance–voltage characteristics were recorded under a forward bias using a computer-controlled Keithley 2400 source meter and a PR650 spectrometer.

2.2. Materials

2-Bromofluorene (**1**), 2,7-dibromofluorene, 9H-carbazole, diphenylamine, 3-methyldiphenylamine, benzyl triethyl ammonium chloride, potassium carbonate, copper powder, 18-crown-6, Pd₂(dba)₃, (*t*-Bu)₃P, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), tris(2-phenylpyridine) iridium (III) {Ir(ppy)₃} and sodium *tert*-butoxide were purchased from Aldrich. 3-Bromomethyl-3-methyl-oxetane was bought from Chemada Fine Chemicals (Israel). All the chemicals were used without further purification.

2-Bromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**2**) was prepared by the reaction of 2-bromofluorene (**1**) with 3-bromomethyl-3-methyl-oxetane in a two-phase system [10,11]. 2-Bromofluorene (5.0 g, 20 mmole) and benzyl triethyl ammonium chloride (0.2 g, 0.92 mmole) were dissolved in DMSO (20 ml), and 20 ml of a sodium hydroxide aqueous solution (50%) were added. In 5 min, 3-bromomethyl-3-methyl-oxetane (8.42 g, 50 mmole) was added dropwise into the reaction mixture. The two-phase system was stirred at 80°C for 6 h under argon. After the TLC control, the reaction mixture was treated with 2 N HCl, and the product was extracted with chloroform. The organic layer was dried over MgSO₄. After filtration and evaporation of the solvent, the crude product was purified by silica gel column chromatography using ethylacetate/hexane (vol. ratio 1:3) as an eluent. Yield: 5.6 g (68%) of yellow powder.

2,7-Dibromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene was prepared by a similar procedure as monobromo derivative **2**. 2,7-Dibromofluorene (5 g, 15 mmole) and benzyl triethyl ammonium chloride (0.15 g, 0.69 mmole) were dissolved in DMSO (20 ml), and 20 ml of a sodium hydroxide aqueous solution (50%) were added. In 5 min, 3-bromomethyl-3-methyl-oxetane (6.36 g, 37.5 mmole) was added dropwise into the reaction mixture. The two-phase system was stirred at 80°C for 5 h under argon. After the TLC control, the reaction mixture was treated with 2 N HCl, and the product was extracted with chloroform. The organic layer was dried over MgSO₄. After filtration and evaporation of the solvent, the crude product was purified by silica gel

column chromatography using ethylacetate/hexane (vol. ratio 1:3) as an eluent. Yield: 4 g (52.5%) of yellow powder.

2-(9-Carbazolyl)-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**3**). 0.5 g (1.2 mmole) of 2-bromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**2**), 0.6 g (3.6 mmole) of 9H-carbazole, powdered potassium carbonate (0.66 g, 4.8 mmole), copper powder (0.3 g, 4.8 mmole), and 18-crown-6 (0.07 g, 0.24 mmole) were stirred in *o*-dichlorobenzene (15 ml) at 180°C under nitrogen for 18 h. Copper and inorganic salts were filtered off, and the solvent was removed by distillation. After precipitation into hexane, the crude product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 2:1) as an eluent. Yield: 0.5 g (83%).

2-Diphenylamino-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**4**). Pd₂(dba)₃ (11 mg, 0.012 mmole) and (*t*-Bu)₃P (6 mg, 0.03 mmole) were stirred in 25 ml of toluene under nitrogen at room temperature for 10 min. 1 g (2 mmole) of 2-bromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**2**), 0.4 g (2.4 mmole) of diphenylamine and 0.58 g (6 mmole) of sodium *tert*-butoxide were added into the reaction mixture, and it was stirred for 8 h at 80°C. The reaction mixture was cooled and quenched by the addition of ice water. The product was extracted into ethylacetate, and the extract was dried over anhydrous MgSO₄. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. Yield: 0.48 g (39%).

¹H NMR spectrum (300 MHz, CDCl₃, δ , ppm): 7.69–6.9 (m, 16H, Ar), 4.23 (d, 2H, CH₂ of oxetane ring, J = 5.5 Hz), 4.18 (d, 2H, CH₂ of oxetane ring, J = 5.7 Hz), 3.65 (d, 2H, CH₂ of oxetane ring, J = 5.4 Hz), 3.51 (d, 2H, CH₂ of oxetane ring, J = 5.6 Hz), 2.47–2.29 (m, 4H, 2 \times CH₂), 0.50 (s, 6H, 2 \times CH₃).

MS(APCI⁺, 20 V), m/z (%): 502.3 ([M + H]⁺, 100).

2,7-Di(9-carbazolyl)-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**5**). 0.5 g (1 mmole) of 2,7-dibromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene, 1 g (6 mmole) of 9H-carbazole, powdered potassium carbonate (0.96 g, 7 mmole), copper powder (0.25 g, 4 mmole), and 18-crown-6 (0.05 g, 0.2 mmole) were stirred in *o*-dichlorobenzene (15 ml) at 180°C under nitrogen for 12 h. Copper and inorganic salts were filtered off, and the solvent was removed by distillation. After precipitation into hexane, the crude product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:3) as an eluent. Yield: 0.2 g (30%).

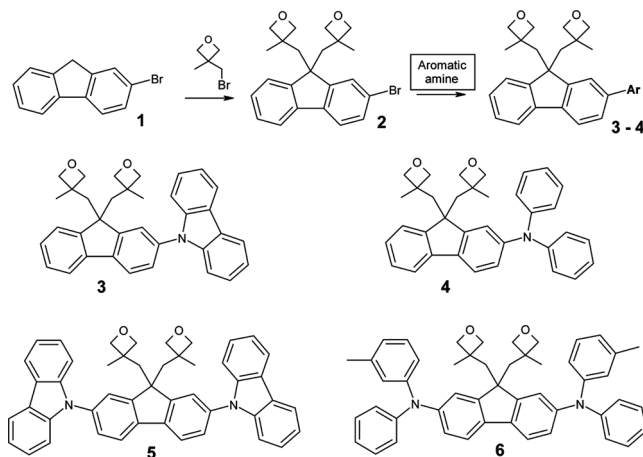
2,7-Di(3-methyldiphenylamino)-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**6**). Pd₂(dba)₃ (11 mg, 0.012 mmole) and (*t*-Bu)₃P (6 mg, 0.03 mmole) were stirred in 25 ml of toluene under nitrogen at room temperature for 10 min. 1 g (2 mmole) of 2,7-dibromo-9,9-di

(3-methyloxetan-3-ylmethyl)fluorene, 0.96 g (6 mmole) of 3-methyldiphenylamine, and 1.15 g (6 mmole) sodium *tert*-butoxide were added into the reaction mixture, and it was heated for 8 h at 80°C. The reaction mixture was cooled and quenched by the addition of ice water. The product was extracted into ethylacetate, and the extract was dried over anhydrous MgSO_4 . The crude product was purified by silica gel column chromatography using ethyl acetate/hexane (vol. ratio 1:2) as an eluent. Yield: 0.55 g (42%).

3. RESULTS AND DISCUSSION

The synthetic route towards the condensed aromatic amines containing the fluorene core with two (photo)polymerizable oxetanyl groups (**3–4**) is shown in Scheme 1. 2-Bromo-9,9-di(3-methyloxetan-3-ylmethyl)fluorene (**2**) as a key material was synthesized from commercially available 2-bromofluorene (**1**) and 3-bromomethyl-3-methyl-oxetane in a two-phase system by a similar procedure as alkylation of fluorene [10,11]. The obtained bromo compound **2** was then treated with 9H-carbazole by the Ullmann reaction [12], or diphenylamine by Buchwald-Hartwig [13,14] palladium-catalyzed amination, respectively, to afford arylamino mono substituted derivatives **3** and **4**. Dicarbazol-9-yl and di(3-methyldiphenylamino) substituted derivatives **5** and **6** were synthesized by the same procedures from commercially available 2,7-dibromofluorene.

All the newly synthesized compounds were identified by mass spectrometry and by ^1H NMR spectroscopy. The data were found to be in



SCHEME 1 Synthesis of fluorene-based compounds **3** and **4**; structures of compounds **3–6**.

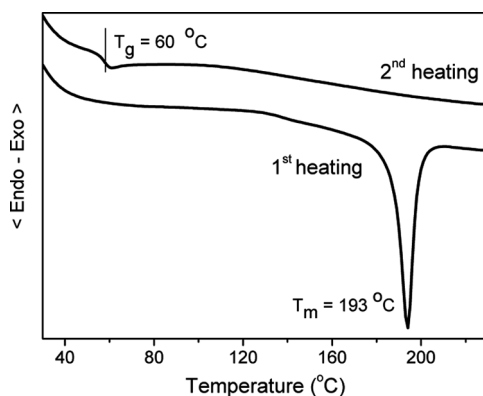
TABLE 1 Thermal Characteristics of Compounds **3–6**

Compound	T_g (°C)	T_m (°C)	T_{ID} (°C)
3	94	209	370
4	60	185	350
5	60	193	300
6	62	157	275

good agreement with the proposed structures. Materials (**3–6**) were soluble in common organic solvents and could form transparent thin films by spin-coating from their solutions.

The behavior under heating of compounds **3–6** was studied by DSC and TGA. The values of glass transition temperatures (T_g), melting points (T_m), and the temperatures at which 5% loss of mass was observed (T_{ID}) are summarized in Table 1. All materials (**3–6**) demonstrated a high thermal stability. The mass loss occurred at temperatures in the range from 275 to 370°C as confirmed by TGA.

All compounds **3** were crystallized after purification and obtained as crystalline materials. When their samples were heated, T_m were observed in the range 157–209°C (Table 1), however the materials readily formed glasses, when their melt samples were cooled on standing in air or with liquid nitrogen. As an example, the DSC thermograms of **5** are shown in Figure 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 193°C. When the melt sample was cooled down and heated again, the glass-transition phenomenon was observed at 60°C, and no peaks due to crystallization and melting appeared on the further heating.

**FIGURE 1** DSC curves of the material **5**. Heating rate – 10°C/min.

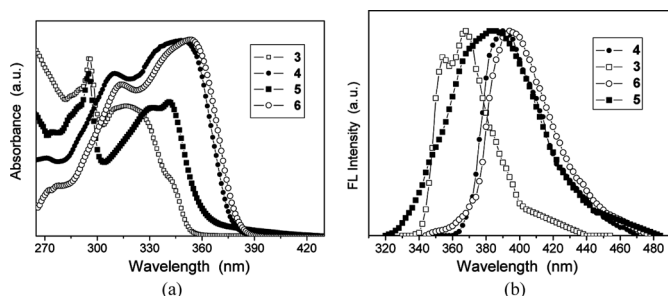


FIGURE 2 UV absorption (a) and FL emission (b) spectra of **3–6** dilute THF solutions.

UV absorption and FL spectra of dilute solutions of the compounds synthesized were recorded. The pertinent data are presented in Figure 2. The electronic absorption energy of the derivatives is similar, and the λ_{max} values are in the range 290–360 nm. Their FL emission maxima appear in the region of wavelengths from 350 to 395 nm. The comparison of the UV absorption and FL spectra of monosubstituted derivative **3** and **4** with those of corresponding disubstituted derivatives **5** and **6** revealed a small bathochromic shift of the spectra of the disubstituted compounds. The bathochromic shift of the spectra indicates different conjugations of derivatives **5** and **6**, and layers of the compounds are expected to show the lower ionization potentials (I_p) than those of **3** and **4**.

Triplet energies (i.e., the transition energy of $T_1 \rightarrow S_0$) of the synthesized materials were estimated from their highest energy phosphorescence peaks at 77 K. Carbazolyl substituted fluorenes (**3** and **5**) have large triplet energies of ~ 2.73 eV. Diphenylamino substituted derivatives (**4** and **6**) show a small red shift in phosphorescence, leading to a lower triplet energy of 2.57 eV. Such triplet energies are large enough for the use of materials **3–6** as hosts for green and red electrophosphorescence, including their use for confining triplet excitons to phosphorescent dopants and for preventing the reverse energy transfer.

The electron photoemission spectra of layers of the compounds synthesized are presented in Figure 3. The values of I_p of the materials range from 5.62 to 5.8 eV. It is evident that the charge injection properties of the synthesized materials depend on the nature of substituents connected to the fluorene core. Diphenylamino substituted derivatives demonstrate lower I_p than those with carbazolyl fragments (cf. I_p of **3** with that of **4** or I_p of **5** with that of **6**). On the other hand, disubstituted fluorenes have lower I_p than those of monosubstituted

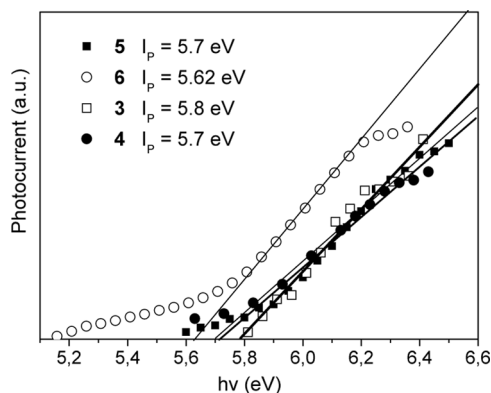


FIGURE 3 Electron photoemission spectra of layers prepared using **3–5**.

derivatives (cf. I_p of **3** with that of **5** or I_p of **4** with that of **6**) probably due to different conjugations, as it was observed from UV absorption and FL spectra.

Derivatives **3** and **6** were tested as host materials in the mixture (7:3) with electron transporting derivative PBD. Commercially available tris(2-phenylpyridine) iridium $\{\text{Ir}(\text{ppy})_3\}$ was used as a guest. The electro-phosphorescent OLEDs were of the following configuration: ITO/PEDOT/host with $\text{Ir}(\text{ppy})_3$ (2 wt. %)/(Ca/Al). The emitting layers were made by spin-coating from the host mixture (**3** or **6** with PBD) containing the guest. When a positive voltage was applied to the device, bright green electro-phosphorescence of $\text{Ir}(\text{ppy})_3$ was observed with the emission maximum at around 510 nm, suggesting the confinement of triplet excitons on triplet dopants.

Figure 4 shows the current–voltage and luminance–voltage characteristics of the OLEDs containing host systems with **3** or **6**. The turn-on voltage of the device containing host of **6** was rather high, and the maximum brightness reached only 240 cd/m^2 . For the device having host of **3**, the turn-on voltage decreased to 13 V. The EL efficiency of the device reached 3.4 cd/A , and the maximum brightness exceeded 1700 cd/m^2 . It should be pointed out that these characteristics were obtained in a non-optimized test device under ordinary laboratory conditions. The device performance may be further improved by both the optimization of the host system and the injection of holes and electrons into the emitting layer. The OLEDs containing cross-linked layers of the materials will be reported later.

In conclusion, cross-linkable carbazol-9-yl or diphenylamino substituted fluorenes have been synthesized and characterized. All the

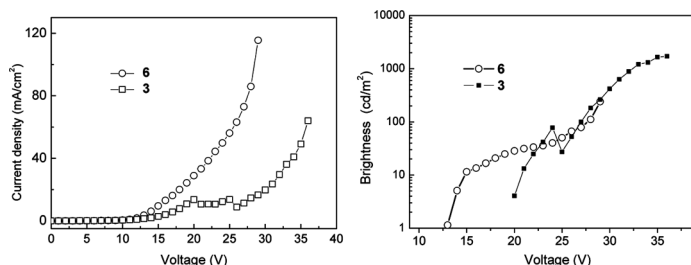


FIGURE 4 OLED characteristics of the device ITO/PEDOT/host with Ir(p-py)₃/(Ca/Al). The host system contains the materials **3** or **6**, respectively.

materials are thermally stable and form amorphous films with glass transition temperatures in the range 60–94°C. The ionization potentials of amorphous layers of the materials depend on their chemical structure and range from 5.62 to 5.8 eV. All the synthesized materials have large triplet energies of 2.57–2.73 eV and are suitable as hosts for green and red phosphorescent light emitting diodes. The device fabricated with the use of one of the new hosts reached a brightness of 1700 cd/m² and a current efficiency of 3.4 cd/A.

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