Novel Soluble Fluorene–Thienothiadiazole and Fluorene–Carbazole Copolymers for Optoelectronics

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Summary: Optical, photophysical, electrochemical and photoelectrical properties of novel soluble low-bandgap fluorene – thienothiadiazole based copolymers (**CHTF** and **CDTF**) and luminescent fluorene – carbazole copolymers, (**CFCzE** and **CFCZA**) were studied. Fluorene – thienothiadiazole copolymers exhibit in thin films long-wavelength absorption with maxima at 750 – 785 nm and possess low bandgap, high electron affinity and exhibit reversible electrochromic behaviour. Therefore they are of interest for electrochromic and photovoltaic applications. Spectroelectrochemical study was performed and optical switching was demonstrated. Photovoltaic devices with bulk heterojunction made of blends of copolymers and fullerene derivative **[60]PCBM** were prepared. The power conversion efficiency was 2–3%. On the other hand, the fluorene-carbazole copolymers exhibit blue photoluminescence with high quantum efficiency in solution and also in thin films. Light-emitting devices with intensive broad bluish-green-white emission were fabricated.

Keywords: conjugated polymers; electroluminescence; fluorene–carbazole copolymers; fluorene–thienothiadiazole copolymers; photovoltaic; spectroelectrochemistry

Introduction

π-Conjugated polymers[1], such as polyphenylenes, polythiophenes, polyfluorenes, fluorene-thiophene copolymers, polycarbazoles, and their modifications **a**re extensively investigated due to their potential use in optoelectronics including light-emitting devices, photovoltaic cells, thin-film transistors, electrochromic devices, and switches.[1] Polythiophenes and thiophene-containing copolymers are promising particularly for photovoltaic applications.[2] Recently, we have prepared new soluble low-bandgap alternating donor-acceptor copolymer (**CTF** in Figure 1) consisting of 9,9-bis(2-ethylhexyl)fluorene and 4,6-di(2-thienyl)thieno[3,4-c][1,2,5]thiadiazole, which we used due to its long wavelengths absorption (maximum at 620 nm) and the electron-acceptor nature of its central thienothiadiazole moiety.[3] We succeeded in the synthesis of new soluble low-bandgap copolymers **CHTF** and **CDTF** consisting of 9,9-bis(2-ethylhexyl)fluorene and 3,3''-dialkyl derivatives of 4,6-di(2-thienyl)-thieno[3,4-c][1,2,5]thiadiazole. These polymers have higher molecular weights, better solubility and thin film processability. In this contribution, we deal with optical, spectroelectrochemical and photovoltaic properties of these copolymers and their blends with fullerene derivative **[60]PCBM**, which were tested in photovoltaic devices. We also report on the photophysics and electroluminescence of fluorene – carbazole copolymers (see Figure 1).

Experimental Part

Copolymers **CHTF** and **CDTF** were prepared by the Suzuki coupling of 9,9-bis(2-ethylhexyl)-2,7-bis(1,3,2-dioxaborinan-2-yl) fluorene with 4,6-bis(5-bromo-3-hexyl-2-thienyl)thieno[3,4-*c*][1,2,5]thiadiazole and

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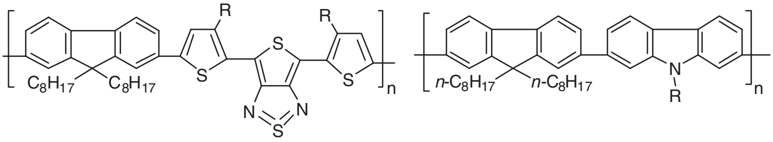

CTF (R = H), **CHTF** (R = C_6H_{13}), **CDTF** (R = $C_{12}H_{25}$)

CFCzE (R = $CH_2CH_2COOCH_3$), **CFCzA** (R = CH_2CH_2COOH

Figure 1.
Chemical structure of the copolymers under study.

4,6-bis(5-bromo-3-dodecyl-2-thienyl)thieno[3,4-*c*][1,2,5]thiadiazole, respectively. Average molecular weights of **CHTF** and **CDTF** were $M_w = 8\ 900$, $M_n = 4\ 860$, and $M_w = 73\ 800$, $M_n = 29\ 020$, respectively. The fluorene-carbazole copolymer **CFCzE** was synthesized by the Suzuki coupling of 9,9-dioctyl-2,7-bis(1,3,2-dioxaborinan-2-yl) fluorene and the methyl 3-(2,7-dibromocarbazol-9-yl)propionate. The copolymer **CFCzA** was obtained by alkaline hydrolysis of **CFCzE** with methanolic sodium hydroxide. Average molecular weight of **CFCzE** was $M_w = 18\ 500$, $M_n = 8\ 400$. Detailed syntheses of monomers and polymers are described in our papers.[3–5] Fullerene derivative [60]PCBM was purchased from Sigma Aldrich.

Thin polymer films were prepared by spin coating. Thin films of **CHTF** and **CDTF** and their blends with **[60]PCBM** were spincoated from 1,2-dichlorobenzene solutions, thin films of **CFCzE** and **CFCzA** from toluene and THF solutions, respectively. All solutions were filtered with 0.45 μm Millex-FH_{13} Millipore syringe filters prior to spin-coating. Thin films for optical studies were spin-coated onto fused silica substrates. For polymer photovoltaic (PV) devices or light-emitting-devices (LEDs), polymer layers were prepared on indium-tin oxide (ITO) substrates covered with a thin layer of poly[3,4-(ethylenedioxy)-thiophene]/poly(styrenesulfonate) (PEDOT:PSS). The ITO glass substrates were purchased from Merck (Germany) and PEDOT:PSS (Baytron PH500) from HC Starck AG (Germany). The 50 nm thick PEDOT:PSS layers were prepared by spin coating and dried in air at 396 K for 15 min. The lithium fluoride (1 nm) or calcium (20 nm) and subsequently 60-80 nm thick aluminum electrodes were vacuum-evaporated on the top of polymer films to form PV or LED devices. Typical active areas of the PV and LED devices were 12 and 4 mm^2, respectively. All polymer films were dried in vacuum (10^{-3} Pa) at 323 K for 6 h. Layer thicknesses were measured using a KLA-Tencor P-10 profilometer. All thin film preparations and the device fabrication were done in glove box under nitrogen atmosphere.

UV-vis spectra were measured on a Perkin-Elmer Lambda 35 UV/VIS spectrometer and photoluminescence (PL) spectra using Perkin-Elmer LS55 Fluorescence spectrometer. Absorption spectra were recorded in the glove box using fiber optics connected to the Lambda 35 UV/VIS spectrophotometer. Current - voltage characteristics of PV devices were measured using the Keithley 237 source measure unit. A 300 W xenon lamp (Oriel) with a filtr WG35 was used for illumination. The light intensity was checked by radiometer Rs 3960 (Laser precision corp.). LEDs were supplied from a Keithley 237 source measure unit, which served for the simultaneous recording of the current passing through the sample. Current-voltage and electroluminescence (EL) intensity-voltage characteristics were recorded simultaneously using a Keithley 237 source measure unit and a silicon photodiode with an amplifier (EG&G HUV-4000B) for detection of total light output. EL spectra were recorded using a Spectra Pro 300i monochomator/spectrograph (Acton Research) with single photon-counting detection

(RCA C31034 photomultiplier). All measurements were performed under nitrogen atmosphere.

Results and Discussion

Fluorene-Thienothiadiazole Copolymers

Absorption spectra of thin layers of the copolymers are shown in Figure 2. The absorption bands with maxima at about 455–475 nm can be assigned to the lowest π-π^* transitions, whereas the lowest-energy absorption (750–785 nm) to the intrachain charge-transfer (ICT) transition between the thiophene donor and thienothiadiazole acceptor moiety. The long-wavelength maximum position and the value of the absorption coefficient depended on the film thickness. An example of absorption for **CDTF** films of two various thicknesses is also shown in Figure 2. An increase in the film thickness indicated decrease in absorption coefficient and blue-shift of the longest wavelength maximum. In the spectra of **CHTF** films the absorption maxima were located at 466 and 772 nm for 44 nm-thick film and blue-shifted (at 454 and 757 nm) for 158 nm-thick film. Similarly in the spectra of **CDTF** films, the maxima were at 472 and 783 nm for 44 nm-thick film, at 465 and 771 nm for 97 nm thick layer and at 463 and 759 nm for the 173 nm film thickness. This result indicates formation of supramolecular structure in thin films due to the strong intermolecular interactions. The similar value of the optical bandgap $E_g^{opt} = 1.36$ eV was determined from the absorption edge of thin film spectra.

The results of electrochemical study showed that both copolymers oxidized and reduced reversibly. The typical cyclic voltammetry (CV) curves of thin copolymer films showed two clear p- and n-doping peaks followed by corresponding un-doping peaks. The ionization potential E_{IP}(HOMO) and the electron affinity E_A (LUMO) were determined from the onsets of the first oxidation and reduction peaks. Similar values of ionization potential at about 5 eV and electron affinity at about 3.5–3.6 eV were evaluated for both copolymers. The values of bandgap evaluated from the onset potentials, 1.4 eV for **CHTF** and 1.5 eV for **CDTF,** were similar to the optical bandgap values. Electrochromic behaviour was observed. The color changes upon reduction and oxidation were studied by spectroelectrochemical measurements.

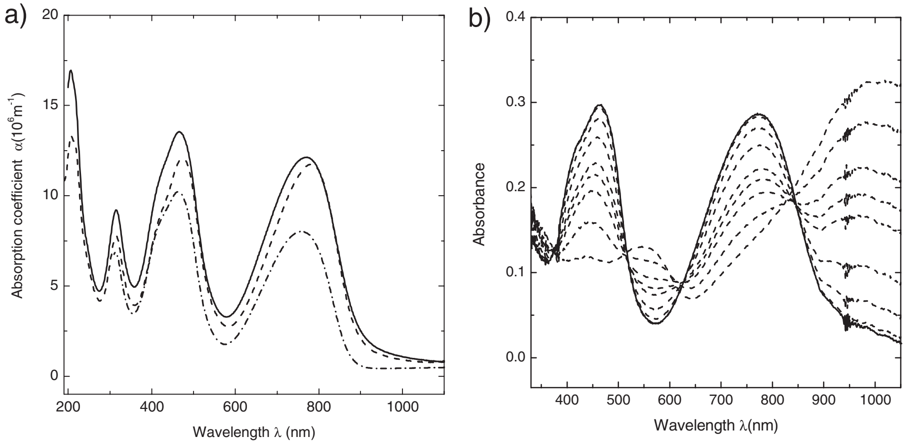

Figure 2.
(a) Absorption spectra of thin films of **CHTF** (solid) and **CDTF** (dashed) with comparable 44 nm thickness, and 173 nm-thick film of **CDTF** (dashed and dotted) prepared on fused silica substrate. (b) Absorption spectra of the copolymer **CHTF** measured in thin film on ITO during the oxidation cycle in situ changing stepwise the voltage from 0 to 0.55 V.

Spectral changes during the oxidation are characterized by a decreasing absorption in visible region and increasing absorption in NIR as is shown in Figure 2b for **CHTF** thin layer spin-coated on ITO substrate. A stable optical switching was demonstrated at the wavelength of 1000 nm for both copolymers. An example is shown in Figure 3 for **CDTF** thin layer on ITO.

The copolymers are promising for photovoltaic application due to the low bandgap, high electron affinity and reversible redox properties. Photovoltaic devices with a bulk heterojunction were prepared from polymer blends with fullerene derivative **[60]PCBM**. Absorption spectra of 125 nm thick blend layers, corresponding to the thickness of the active layer in PV device, are shown in Figure 4. Absorption maxima are located at 331, 458 and 761 nm for the **CHTF:[60]PCBM**, and at 462 and 768 nm for **CDTF:[60]PCBM**, similarly as in the spectra of neat copolymer thin films. Due to the **[60]PCBM** content the UV absorption increased and absorption in visible region decreased compared with the neat thin film (compare with dotted curve).

Two types of photovoltaic (PV) devices with LiF/Al and Ca/Al electrodes were prepared. Typical dark and photovoltaic current-voltage characteristics are shown in Figure 5 for the devices with the best performance. PV devices with **CHTF:[60]PCBM** active layer showed higher power conversion efficiency η for LiF/Al electrode, while using **CDTF:[60]PCBM** as an active layer the best results were obtained with Ca/Al electrode giving power conversion efficiency up to 3%. The characteristic data are summarized in Table 1.

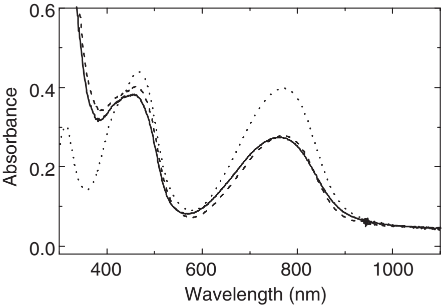

Figure 4.
Absorption spectra of 125 nm-thick films made of **CHTF:[60]PCBM**(1:1) (solid), **CDTF:[60]PCBM**(1:1) (dashed) on fused silica substrate and 100 nm-thick **CDTF** film (dotted) for comparison.

Luminescent Fluorene – Carbazole Copolymers

Typical absorption and PL of thin films made of both **CFCzE** and **CFCzA** are displayed in Figure 6. Absorption maxima corresponding to the backbone conjugation were located at 383 and 379 nm in **CFCzE** and **CFCzA** thin films, respectively. Thin films of both copolymers exhibited a similar

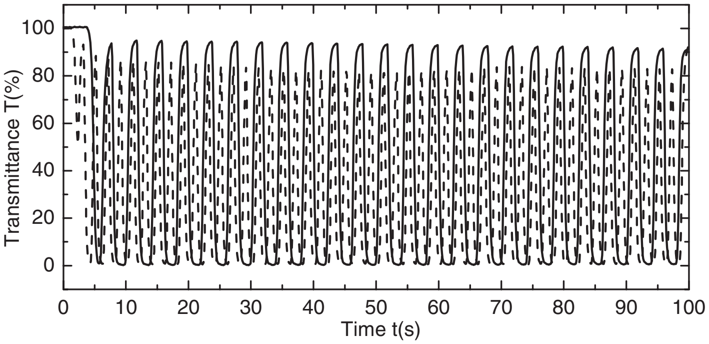

Figure 3.
Changes of the transmittance measured for **CDTF** thin film on ITO substrate during the switching between neutral and oxidized state (0 and 0.7 V, respectively) detected at 1000 nm for different switching time 2s (solid) and 1s (dashed).

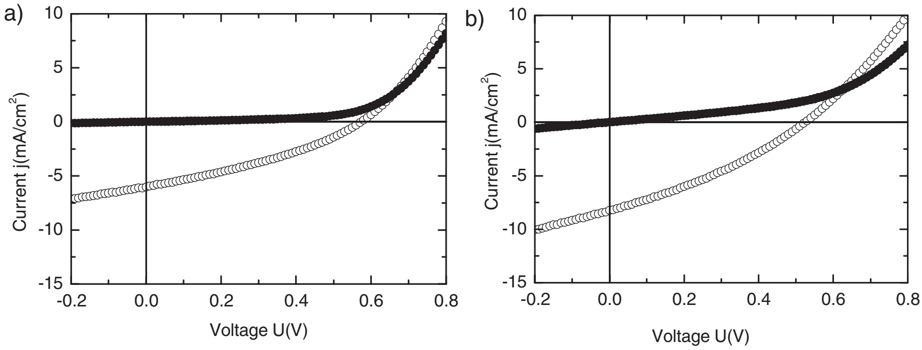

Figure 5.
Current-voltage characteriscics PV devices (a) ITO/**PEDOT:PSS/CHTF: [60]PCBM**/LiF/Al and (b) ITO/PEDOT:PSS/**CDTF:[60]PCBM**/Ca/Al measured in dark (solid circles) and under illumination 45 mW/cm^2 (open circles).

Table 1.
Photovoltaic characteristic data measured at illumination with Xe lamp with UV filtr WG35 for 45 mW cm^{-2}

PV device	U_{OC} (V)	I_{sc} (mAcm^{-2})	*FF* (%)	η (%)
ITO/PEDOT:PSS/**CHTF:[60]PCBM**/LiF/Al	0.575	6.05	33.5	2.59
ITO/PEDOT:PSS/**CHTF:[60]PCBM**/Ca/Al	0.46	6.21	27	1.72
ITO/PEDOT:PSS/**CDTF:[60]PCBM**/LiF/Al	0.485	7.85	27.5	2.33
ITO/PEDOT:PSS/**CDTF:[60]PCBM**/Ca/Al	0.525	8.25	32	3.07

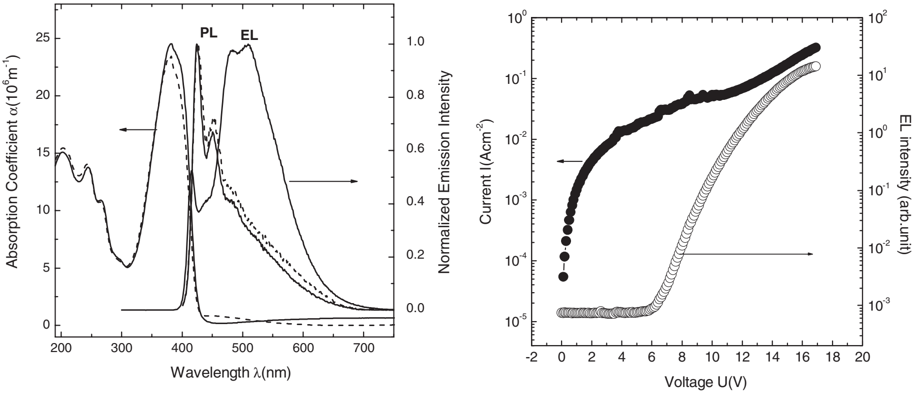

Figure 6.
Absorption and photoluminescence spectra of **CFCzE**(solid) and **CFCzA**(dashed) thin films. EL spectrum and current-voltage and EL intensity-voltage dependences of LED made of **CFCzE** (ITO/PEDOT:PSS/**CFCzE**/Ca/Al). device.

PL spectra shape with a vibration structure (main maximum at about 425 nm) and a long-wavelength tail up to 650 nm. The relative value of PL efficiency in thin **CFCzE** films was ca 3 times higher than that of **CFCzA**. The PL long-wavelength tail indicated excimer or aggregate formation.

The long-wavelength emission dominated in EL. Efficient LEDs with EL maximum at about 480-510 nm have been fabricated. An example of a EL spectrum of ITO/PEDOT:PSS/**CFCzE**/Ca/Al LED is also shown in Figure 6. The onset of the EL emission was at about 5×10^7 V m^{-1}. Typical dependences of the current and the

EL intensity on the applied voltage measured on the ITO/PEDOT:PSS/**CFCzE**/Ca/Al LEDs are shown in Figure 6. In our LEDs EL efficiency values up to 3 cd/A were achieved.

Conclusion

Soluble fluorene – thienothiadiazole copolymers exhibit in thin films long-wavelength absorption with maxima at 750–785 nm significantly red-shifted compared to those in solution due to strong intermolecular interactions in solid state. They possess low bandgap, high electron affinity and exhibit reversible electrochromic behaviour, stability of which was demonstrated by optical switching. Therefore they are of interest for electrochromic and photovoltaic applications. Spectroelectrochemical study showed the optical spectral changes during oxidation - a decrease in absorption in visible region and an increase in NIR absorption. Reversible optical switching was demonstrated by transmittance measurements. We succeeded in fabrication of PV devices with bulk heterojunction made of blends of **CHTF** or **CDTF** with fullerene derivative **[60]PCBM**. The power conversion efficiency was up to 3%. Fluorene-carbazole copolymers **CFCzE** and **CFCzA** exhibited blue photoluminescence with high quantum yield in solution. Thin films exhibited intense blue photoluminescence with a tail up to 650 nm. Light-emitting devices with intensive broad blue-green-white emission were fabricated. LEDs made of **CFCzE** exhibited better performance and EL efficiency up to 3 cd/A than those made of **CFCzA**.

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