

# PHOTOLUMINISCENCE PROPERTIES OF THE POLYTHIOPHENE-FULLERENE SYSTEM

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*Received 19 May 2017; accepted 25 May 2017*

## 1. Introduction

Polymer solar cells belong to the solar cells of third generation. They are generally flexible, due to the polymer substrate. Each polymer solar cell contains donor and acceptor units. Conjugated polymer or small organic molecules is most widely used as the donor and fullerene derivatives are used as the acceptor material [1]. When the donor and the acceptor material are brought into contact, the result is the so-called heterojunction and this is a basis for the operation of organic solar cells [2–4]. However, the experiments show that when a suitable polymer is being developed and the model devices based on such a polymer show high efficiencies, it is still a great practical and technological challenge to transfer the device structure to a process in large scale production.

The studied system consists of a donor molecule of polythiophene–polyoxyethylene copolymer with acceptor molecules [6,6]-phenyl-C<sub>61</sub> butyric acid butyl ester and [6,6]-phenyl-C<sub>61</sub> butyric acid octyl ester. Fluorescence spectroscopy was used to study the effect of fluorescence quenching after the formation of an excited-state complex between polythiophene–polyoxyethylene copolymer and fullerene.

## 2. Experimental Details

Synthesis of polythiophene-polyoxyethylene copolymer (PTHPEO copolymer) was performed by condensation reaction of dimethyl ester of 3,3''-bis decyl [2,2'; 5',2''; 5'',2'''; 5''',2''''; 5''''',2'''''] sexithiophene-5,5''''-dicarboxylic acid with polyethylene oxide [5]. The molecular weight of PTHPEO copolymer was approximately 15 000 a. u. The solution of copolymer in chloroform was prepared by ultrasonic dissolution in the concentration of 0.44 g/l. [6,6]-phenyl-C<sub>61</sub> butyric acid butyl ester (PCBB) and [6,6]-phenyl-C<sub>61</sub> butyric acid octyl ester (PCBO) were purchased from Sigma-Aldrich. The solutions of PCBB and PCBO in chloroform were prepared by ultrasonic dissolution in the concentration of 1.0 g/l.

The absorption spectra were recorded using UviLine 9100 single-beam spectrophotometer with a halogen light source operated at optical resolution of 4 nm with a measuring range from 320 to 1100 nm. All absorption spectra were measured at room temperature.

The fluorescence excitation and emission spectra at room temperature were performed by Horiba Jobin-Yvon SPEX Fluorolog-3 with the 450 W Xe lamp, the 90° configuration, with the entrance and exit slits of 1 nm bandpass, the integration time was 0.1 s.

In the photochemical quenching, the samples were exposed by a 100 W broad-band halogen lamp with an IR thermal filter. Collimating lens with the focal length of 50 mm ensured uniform illumination of the cuvettes. The exposure time was 20 minutes.

### 3. Results and Discussion

Absorption spectrum of the PTHPEO copolymer in chloroform (Fig.1) was measured to determine value of the absorption maximum wavelength. It results that the copolymer shows  $\lambda_{\max}$  at 437 nm. This result is in agreement with [6] and also with  $\lambda_{\max}$  in excitation spectrum of the PTHPEO copolymer in chloroform. The PTHPEO copolymer in chloroform has the emission maximum in the green region,  $\lambda_{\max} = 528$  nm. These values were used for fluorescence measurements of the PTHPEO copolymer and PCBB/PCBO complexes. Absorption spectra of both fullerene derivatives in chloroform are shown in Fig. 1. The spectra of PCBB and PCBO show two absorptions at 328 and 432 nm, which are typical of fullerene [6,6]-adducts.

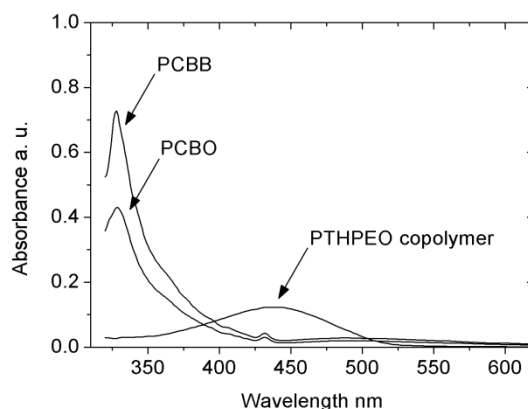


Fig.1: Absorption spectra of polythiophene-polyoxyethylene copolymer (PTHPEO copolymer) in chloroform and [6,6]-phenyl- $C_{61}$  butyric acid butyl ester (PCBB) and [6,6]-phenyl- $C_{61}$  butyric acid octyl ester (PCBO) in chloroform.

The fluorescence emission and excitation spectra of the PTHPEO copolymer with various concentration of PCBO (Fig. 2) were measured to determine optimal concentration range for the photochemical experiment. The concentration of PTHPEO copolymer in solution was constant (0.1 g/l) and the concentration range of PCBO was from 0.3 to 0.7 g/l.

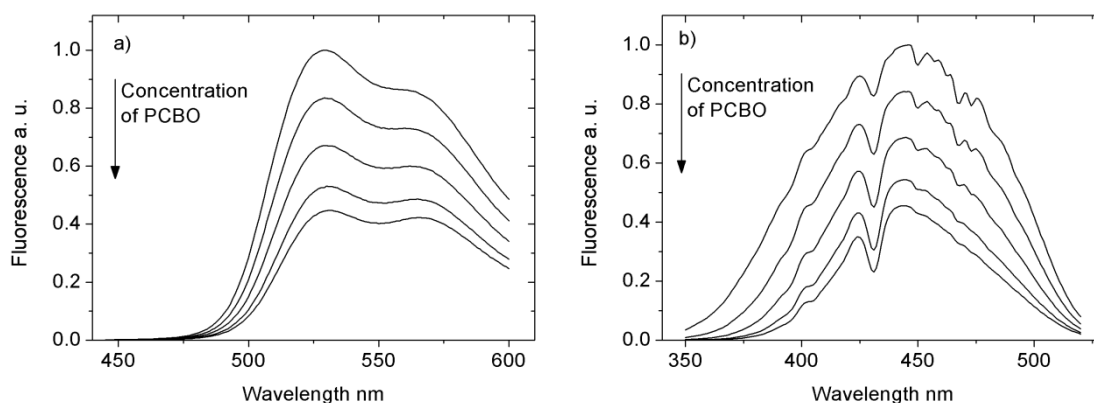


Fig.2: The fluorescence a) emission and b) excitation spectra of polythiophene-polyoxyethylene copolymer (PTHPEO copolymer) and [6,6]-phenyl- $C_{61}$  butyric acid octyl ester (PCBO) in chloroform – effect of PCBO concentration (0.7; 0.6; 0.5; 0.4 and 0.3 g/l). The concentration of PTHPEO copolymer was constant (0.1 g/l).

The aim of work is the study of the effect of excited-state complex formation in the PTHPEO copolymer and PCBB/PCBO solution after light exposure. However, the absorption spectra do not reflect the presence of the excited-state complex, because system is unstable in the ground state after fluorescence. Due to this fact and to fact that the exciplex formation takes place in the excited state, the fluorescence emission spectra were measured. Fig. 3 and 4 show the fluorescence emission and excitation spectra of the PTHPEO copolymer and PCBB/PCBO. In these spectra the isosbestic points were found, which demonstrate the equilibrium between PTHPEO copolymer and PCBB/PCBO. The isosbestic point for both solutions was at wavelength  $\lambda = 508$  nm (Fig. 3–4). In Fig. 3–4 also the quenching of fluorescence was determined. It means the fluorescence was diminished in intensity due to the deactivation of the lowest excited singlet state of the analyte by interaction with other species in solution. In this case, interaction between PCBB/PCBO and PTHPEO copolymer results in the formation of a transient excited complex which is less fluorescent and may be deactivated by any of usual radiationless modes of deactivation of excited singlet states. The presence of the quenching species has no effect on the absorption spectrum of the PTHPEO copolymer.

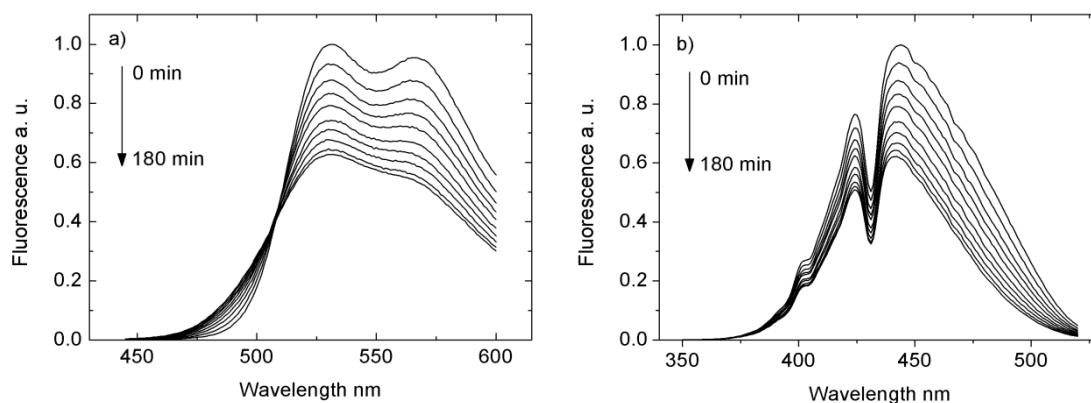


Fig.3: The fluorescence a) emission and b) excitation spectra of polythiophene–polyoxyethylene copolymer and PCBB – effect of light exposure. Time interval of light exposure was 20 minutes.

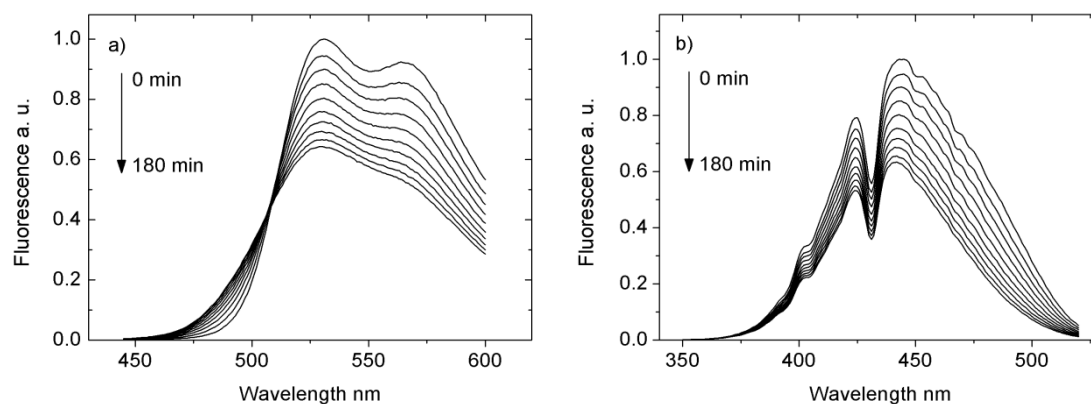


Fig.4: The fluorescence a) emission and b) excitation spectra of polythiophene–polyoxyethylene copolymer and PCBO – effect of light exposure. Time interval of light exposure was 20 minutes.

The effect of light exposure on formation of the excited-state complex was also examined. The solutions of PTHPEO copolymer and PCBB/PCBO were exposed by light during various time intervals (0 – 180 min.). The aim of the experiment was to increase formation of the excited-state complex. Fig. 3 and 4 reveal that the fluorescence was decreased in intensity by 37.3 % for PCBB and 35.9 % for PCBO in 180 minute exposure. This observation proved enhancement of the excited-state complexes after the light exposure. As mentioned above, PCBB/PCBO and PTHPEO copolymer formed transient excited complexes which are less fluorescent and the quenching of fluorescence was observed in the complexes. The influence of fullerene side chain length (butyl/octyl) on the formation of excited complexes was also studied and compared. The significant changes were not observed between fluorescence emission spectra of PTHPEO copolymer with PCBB and with PCBO.

#### 4. Conclusion

The main goal of presented work was investigation of the effect of excited-state complex formation in the PTHPEO copolymer and PCBB/PCBO solution after light exposure. The PTHPEO copolymer creates structurally-organized clusters composed of conducting (oligothiophenic) and non-conducting (PEO) segments in the solid state. Because of this structural attribute, the PTHPEO copolymer has high application potential in polymer solar cells fabrication. Absorption and fluorescence spectra were measured. In emission fluorescence spectra of PTHPEO copolymer and PCBB/PCBO solution the quenching of fluorescence was observed. These results suggest the formation of the excited-state complex between PTHPEO copolymer and PCBB/PCBO.

#### Acknowledgement

This work was financially supported by grant of Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences No. VEGA-1/0501/15 and Cultural and Educational Grant Agency (KEGA) of the Ministry of Education, Science, Research and Sport of the Slovak Republic No. 026STU-4/2015.

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