

Exciton dynamics in polyfluorene containing end-groups with intramolecular charge transfer (ICT) state

E. R. Simas^{(1)*} and M. H. Gehlen⁽¹⁾

(1) Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos-SP, Brasil.

* Corresponding author: simas@iqsc.usp.br

Abstract – Poly(9,9'-di-*n*-octylfluorene) having end-groups with ICT state was prepared by Yamamoto-coupling reaction. The polymer was studied in solution by steady-state and time-resolved fluorescence techniques. It showed a complex exciton dynamics, involving the formation of a coupled excited state between fluorene units of the backbone and ICT state of the end-group. For comparison, a polyfluorene without end-group was prepared as standard.

In this work, poly(9,9'-di-*n*-octylfluorene) (PFO-1) and PFO-1 end-capped with N-(2-benzothiazole)-1,8-naphthalimide (PFO-2) were prepared via Ni(0) mediated Yamamoto-coupling reaction. The end-capper (see Fig.1) was synthesized by the reaction between 4-bromo-1,8-naphthalic anhydride and 2-aminobenzothiazole in dimethylacetamide (DMAc) at 180 °C for 3h. An end-group without bromine atom was synthesized by the same procedure and was used as standard in the photophysical study.

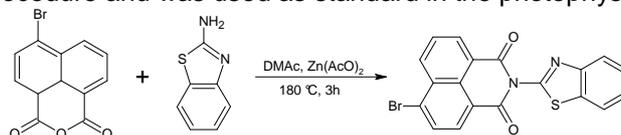


Figure 1: Synthesis of the end-capper used in the preparation of the PFO-2.

The emission of the end-group is affected by solvent polarity; its maximum changes from 408nm in toluene to 464nm in DMSO, indicating the existence of an intramolecular charge transfer (ICT) in the excited state. The photophysical properties of the polymers in solution were investigated by varying solvent polarity. The emission of the two polymers in different solvents is different. In PFO-2 emission spectra, the band at 470nm (which appears as a shoulder in PFO-1) is much more pronounced, and an additional shoulder on 520nm is observed. It suggests the formation of a coupled excited state with mixed character between emissive singlet (fluorene units of the polymer backbone) and ICT (end-group).

Time-resolved studies of the polymers confirm this hypothesis. Triexponential emission decay was found for PFO-2 (with lifetimes of 26-87ps (τ_1), 438-624ps (τ_2) and 1-3ns (τ_3)), in contrast with a single lifetime ($\tau_1=357-472$ ps) fitted for PFO-1. The three lifetimes of PFO-2 are associated with energy migration to the coupled state, backbone emission, and coupled state emission, respectively (see Fig.2). Time-resolved fluorescence anisotropy shows a relaxation time between 102-132ps for PFO-1, ascribed to the reorientation of fluorene units in the polymer backbone. PFO-2, in turn, exhibits biexponential anisotropy decay with decay times of 5-12ps and 669-936ps. The first decay time is in the same time range of the τ_1 decay component, and is faster than the relaxation time observed in PFO-1. This component can be related to the depolarization caused by energy migration from the backbone to the coupled state. The slower component is associated with polymer end segments motions at longer times.

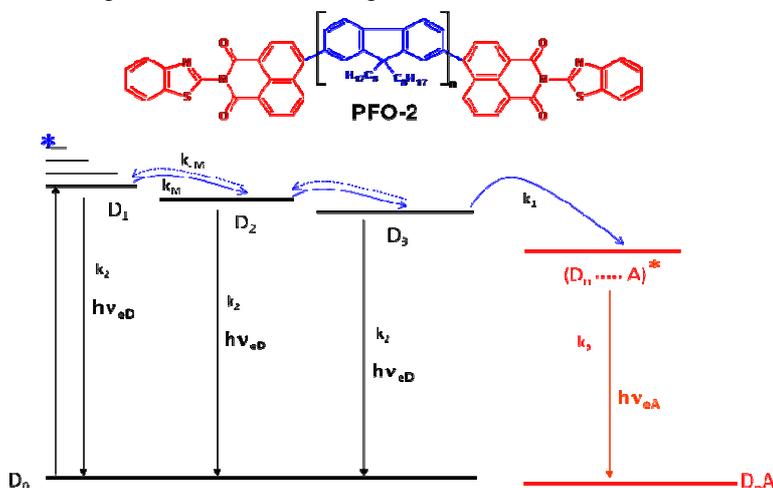


Figure 2: Energy diagram of the electronic states ($D_1 \dots D_n$) of PFO-2, and the decay processes (k_1 , k_2 and k_3) involved in the emission. Where: $k_1 = 1/\tau_1$, $k_2 = 1/\tau_2$ and $k_3 = 1/\tau_3$