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The ultrafast dynamics and nonlinear optical properties of tribranched conjugated polymers with triphenylamine as the core

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Abstract

The nonlinear optical properties and the ultrafast dynamics for the polymers with the donor–acceptor structure were measured by the femtosecond laser spectroscopic techniques. Two polymers show intense two-photon absorption properties due to the unique tribranched structure. The ultrafast dynamics of the excited states were measured by two-color femtosecond pump–probe method, and the relaxation properties of the fluorescence emission state were detected by time-resolved fluorescence (TRFL) technique. We suggest that the fast decay component in the TRFL dynamics comes from the exciton migration process, and the slow decay component is caused by the recombination process of the excitons. In two-color femtosecond pump–probe and TRFL dynamics, both decay processes were accelerated when the solvent was changed from $CHCl_3$ to DMSO, due to the fact that the dipole moment of DMSO is larger than that of $CHCl_3$.

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1. Introduction

Materials with two-photon absorption (TPA) ability have potential applications in various fields, including three-dimensional microfabrication, [1,2] information technology, [3] laser technology, [4] biological system imaging, [5] etc. Several design strategies have been proposed to improve TPA ability, such as building of multibranched molecules with donor (D) and acceptor (A) structure which can significantly enhance TPA response. It was reported that the ratio of TPA cross-sections

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of the tribranched molecules to the monomer was about 6.8 [6]. For minimizing the disperse concentration in the matrix and the phase segregation, peoples catch a sight on how to synthesize the polymers with large TPA property.

In past years, dynamics of the multibranched molecules [7–9] and polymers [10–13] have been measured by different methods for the basic interest of the excited-state behavior and applications. Femtosecond (fs) pump–probe and time-resolved fluorescence (FL) experiments are useful techniques which can be used to obtain the information of the relaxation processes of the excited state and the decay properties of the FL emission state.

In this paper, we report our research results on optical properties and excited-state dynamics of two polymers with tribranched structures. Dynamics of the excited state in different solvents, were measured by two-color pump–probe experiment, and the relaxation processes of the FL emission state were studied by time-resolved fluorescence (TRFL) experiment. The fast decay process observed in two experiments is assigned to the exciton migration and the slow decay time is related to the recombination process of the excitons. The relaxation processes in the pump–probe experiment are accelerated in the solvent DMSO with larger dipole moment than the solvent $CHCl_3$.

2. Materials and experimentals

Two new tribranched phenylene vinylene (HPV1 and HPV2) were designed and synthesized with triphenylamine and long hexyloxy side chain substituted PPV. Two polymers possess D–π–D or D–π–A structures, shown in Fig. 1(a). The triphenylamine served as donor and the nitrobenzene

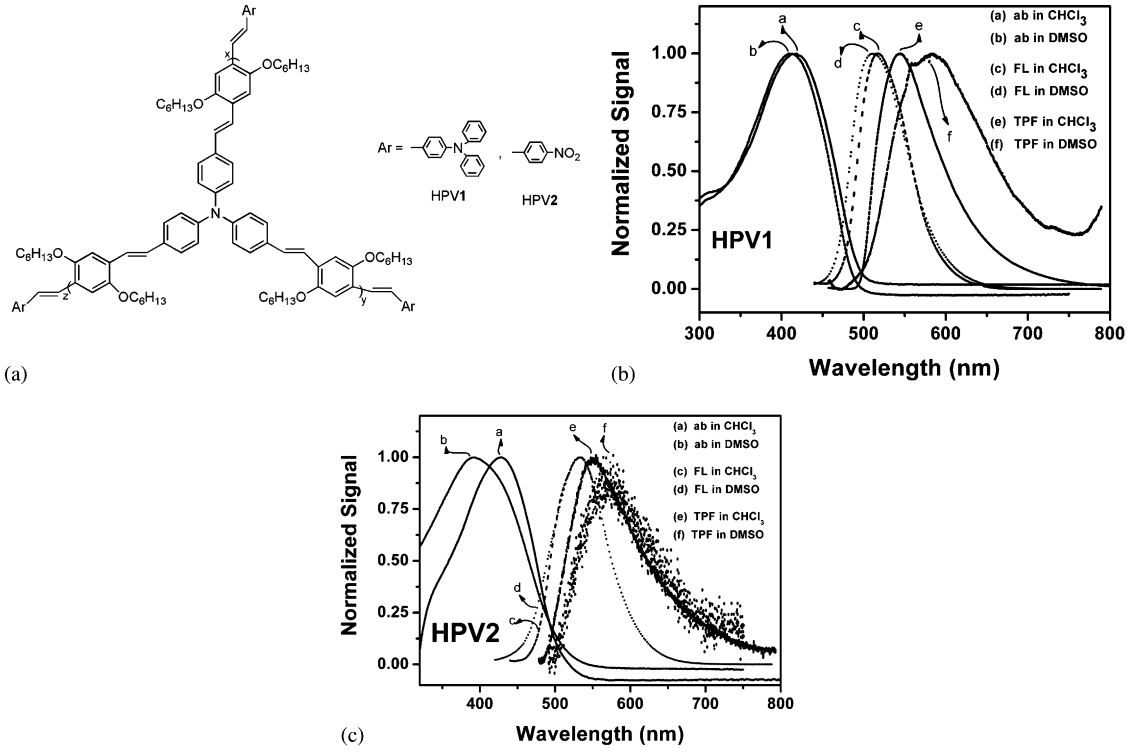

Fig. 1. (a) Molecular structures of HPV1 and HPV2 and (b) and (c) are the normalized one-photon absorption, one-photon fluorescence and TPF spectra in $CHCl_3$ and DMSO for HPV1 and HPV2, respectively.