



Research paper

Acceptor number-dependent ultrafast photo-physical properties of push-pull chromophores using time-resolved methods

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ABSTRACT

Three push-pull chromophores comprising a triphenylamine (TPA) as electron-donating moiety and functionalized β -diketones as electron acceptor units are studied by various spectroscopic techniques. The time-correlated single-photon counting data shows that increasing the number of electron acceptor units accelerates photoluminescence relaxation rate of compounds. Transient spectra data shows that intramolecular charge transfer (ICT) takes place from TPA units to β -diketones units after photo-excitation. Increasing the number of electron acceptor units would prolong the generation process of ICT state, and accelerate the excited molecule reorganization process and the relaxation process of ICT state.

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1. Introduction

Over the past two decades, organic semiconducting oligomers have been considered as the alternatives to their inorganic counterparts for optoelectronic devices such as light emitting diodes [1], field-effect transistors [2], and solar cells [3], owing to their low cost, solution-processed fabrication and flexible devices. In order to obtain excellent photo-physical properties, people gradually design and synthesize many oligomers, composed of electron-donating (D) and electron-accepting (A) groups through π -conjugated linker (with dipole character). To further enhance the absorption section, oligomers with single, double and triple branches are also synthesized [4], which change the symmetry of oligomers and tune their photo-physical properties [5]. Increasing the dimensionality of donor- π -acceptor (D- π -A) molecules gives rise to some special electronic properties compared to the linear counterparts due to extended one-dimensional backbones with delocalized mobile π -electron systems [6–10]. A previous report [11] shows that the D- π -A oligomers often possess the intramolecular charge transfer (ICT) properties, which can form local-

ized or delocalized ICT state after photo-excitation. The ICT state can affect the luminescence behavior of oligomers [12–16], by manipulating the photo-excitation relaxation process of excited oligomers [17,18]. Here, we present a study of three compounds which are composed of triphenylamine (TPA) moiety functionalized β -diketones units.

The molecular structures of three multi-branched push-pull chromophores are shown in Fig. 1, in which the electron donor moieties (TPA) are in the center, with β -diketone units as electron acceptor in each branch. Note that, **1** with a single branch is monomer, **2** with two branches is dimer, and **3** with triple branches is trimer. Previous report [4] shows that the self-assembling properties depend on the molecular structures, however, the relaxation process of ICT state in D- π -A compounds affected by the number of electron acceptor units still remains unclear.

In this paper, we present the spectroscopic characteristics and ultrafast photo-physical properties of three synthesized push-pull compounds (named **1**, **2** and **3**) to understand the relationship between the photoluminescence (PL) property and the number of electron acceptor units. The final results show that increasing the number of electron acceptor units can affect the evolution of ICT state and improve the PL property by regulating the relaxation process of excited compounds.

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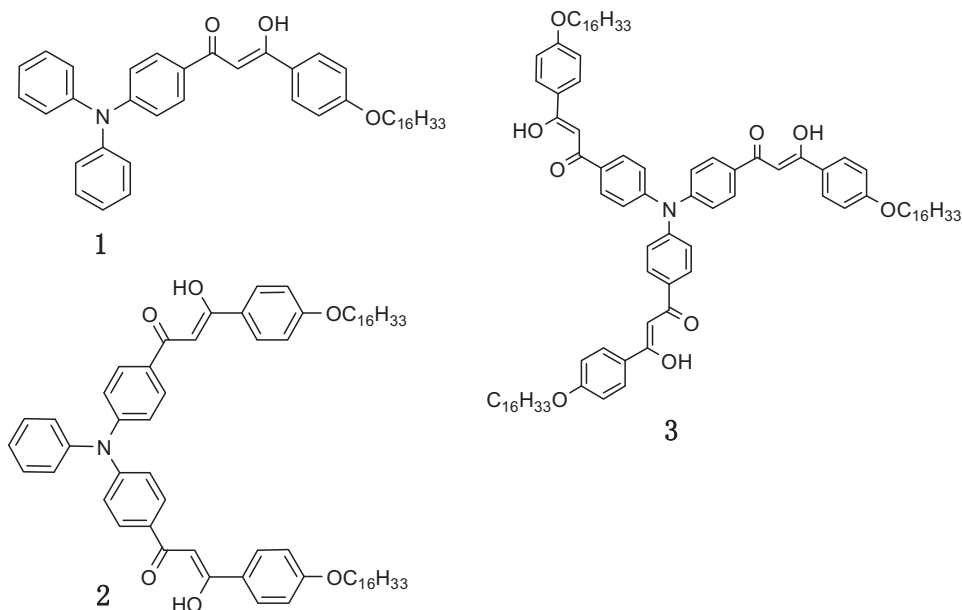


Fig. 1. The molecular structure of compounds **1**, **2** and **3**.

2. Experimental

2.1. Materials

The compounds of monomer (**1**), dimer (**2**), and trimer (**3**) were obtained from Lu's group in college of chemistry in Jilin University. Synthetic procedures of compounds **1**, **2** and **3** were similar to their previous work [4]. The aggregation originated from the high concentration has also been considered before our transient absorption (TA) test. And we choose the concentration as 5×10^{-4} mol/L (See Figs. S1 and S2, Supporting information). The peak position and FWHM (Full Width Half Maximum) of normalized steady absorption and the PL spectra have no change, indicating the concentration in our experiment is reasonable. Furthermore, the excitation intensity dependent kinetic curves measurements results show that the kinetic curves not exhibit exciton–exciton annihilation process in high excitation intensity, indicating that no aggregation exists in TA test at the concentration of 5×10^{-4} mol/L. For the pump-probe measurements, the corresponding optical density (OD) was around 0.6. at 400 nm in a 1 mm path length quartz cuvette.

2.2. Spectral measurements and quantum chemistry calculation

Steady absorption measurements were carried out in UV–Vis absorption spectrometer (Purkinje, TU-1810PC). Photoluminescence (PL) measurements were made with a fiber optic spectrometer (Ocean Optics, USB4000) with an excitation wavelength of 400 nm. The femtosecond transient absorption (TA) technique is reported elsewhere [19]. The excitation spot was about 2.0 mm in diameter. The excitation wavelength was 400 nm. The TA spectrum were carried out by a spectrometer (AvaSpec-2048×16). No photo-degradation was observed after femtosecond TA measurements. The PL dynamics are detected by time-correlated single-photon counting [20] (TCSPC) technique. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 2 shows the normalized steady-state absorption and photoluminescence (PL) spectra of **1**, **2** and **3** dissolved in DMF. All the

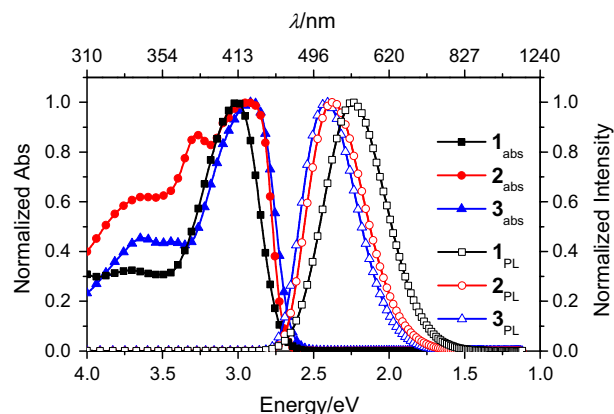


Fig. 2. Normalized steady state absorption and photoluminescence spectra of **1** (black), **2** (red) and **3** (blue) in DMF solution.

compounds in DMF show two absorption peaks and their main absorption peaks are 412 nm (**1**), 422 nm (**2**) and 427 nm (**3**), which are almost independent of the electron acceptor number in the compounds. The detailed spectral data are summarized in Table 1. The high-energy absorption band in the near-ultraviolet region results from π – π^* transition [21]. The quantum chemical calculation results in previous report [4] demonstrated that the π -electron in low highest occupied molecular orbital (HOMO) for compounds **1–3** are mainly delocalized over the TPA units, while lowest unoccupied molecular orbital (LUMO) are mainly delocalized over β -diketone units. Therefore, the low energy absorption band is attributed to the charge transfer between electron donor and electron acceptor [4], [22–25]. In contrast to absorption spectra, the PL spectra of all the compounds are dependent of the number of electron acceptor. Their emission peaks are located at 552 nm (**1**), 522 nm (**2**) and 512 nm (**3**), exhibiting significant blue shifts with the increasing of electron acceptor number. The Stokes shifts are 6156 cm^{-1} (**1**), 4540 cm^{-1} (**2**) and 3888 cm^{-1} (**3**), respectively. It significantly decreases with increasing the branch number, indicating the remarkable reorganization and the intermolecular charge transfer between electron donor and electron

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