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Ultrafast energy transfer in dansylated POPAM–eosin complexes

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Abstract

Excitation energy transfer (EET) in dendritic host–guest complexes has been studied. Three generations G2, G3 and G4 of dansyl substituted poly(propyleneamine) dendrimers (POPAM) were complexed with a fluorescent dye eosin in chloroform solution. Arrival of excitation from dansyls to eosin was monitored by femtosecond transient absorption spectroscopy. EET rates from the dansyls to eosin(s) are characterised by two time constants 1 ps and 6 ps independent of dendrimer generation. Relaxation processes in eosin were clearly faster when complexed with dendrimer than in solution. As several eosins are bound to G3 and G4 dendrimers, besides host–guest interaction, also eosin–eosin interactions may contribute to the faster relaxation observed in these complexes.

1. Introduction

Dendrimers are multi-branched (macro-)molecules often with highly symmetric structure. They can act as hosts for guest molecules capable of binding via non-covalent interactions such as van der Waals interaction or hydrogen bonding [1,2]. Dendrimers can be functionalized with various functional groups and hence allow design of several novel applications, such as directional excitation energy transfer at molecular level [3]. Presence of several chromophores in a single dendrimer incurs high absorption coefficient of the molecule. This allows efficient collection of optical energy, making dendrimers potential candidates for light harvesting applications [4]. In order to make absorbed light energy usable it has to be collected from the antenna system to an acceptor. Acceptors can be covalently linked to a donor or they can be associated to a donor via van der Waals interactions. Loose binding offers an interesting new possibility, the acceptor may be changed or removed without affecting the donor. We have studied a donor acceptor system, where poly(propylene amine) dendrimers (POPAM) functionalized with dansyl chromophores are acting as donors and eosin molecules supramolecularly bound to a POPAM serve as acceptors [5].

As energy transfer processes occur in timescales of picoseconds or even femtoseconds, ultrafast techniques are needed to study their detailed kinetics. Excitation energy transfer in dendrimers where the acceptor is covalently bound to the dendrimer has been studied by femtosecond techniques [6–10]. In the present letter results on excitation energy transfer are reported in host–guest systems containing from one to several non-covalently bound acceptor molecules per dendrimer.

2. Experimental

Dansylation of POPAM dendrimers used in this study have been described elsewhere [11,12]. The structural formula of third generation dansylated POPAM (called G3 from now on) is shown in Fig. 1. All dendrimer samples were dissolved in chloroform. Eosin was dissolved in ethanol. The two solutions were brought together and after rigorous mixing eosin disappears from the ethanol phase and is transferred to the chloroform phase, a clear indication of

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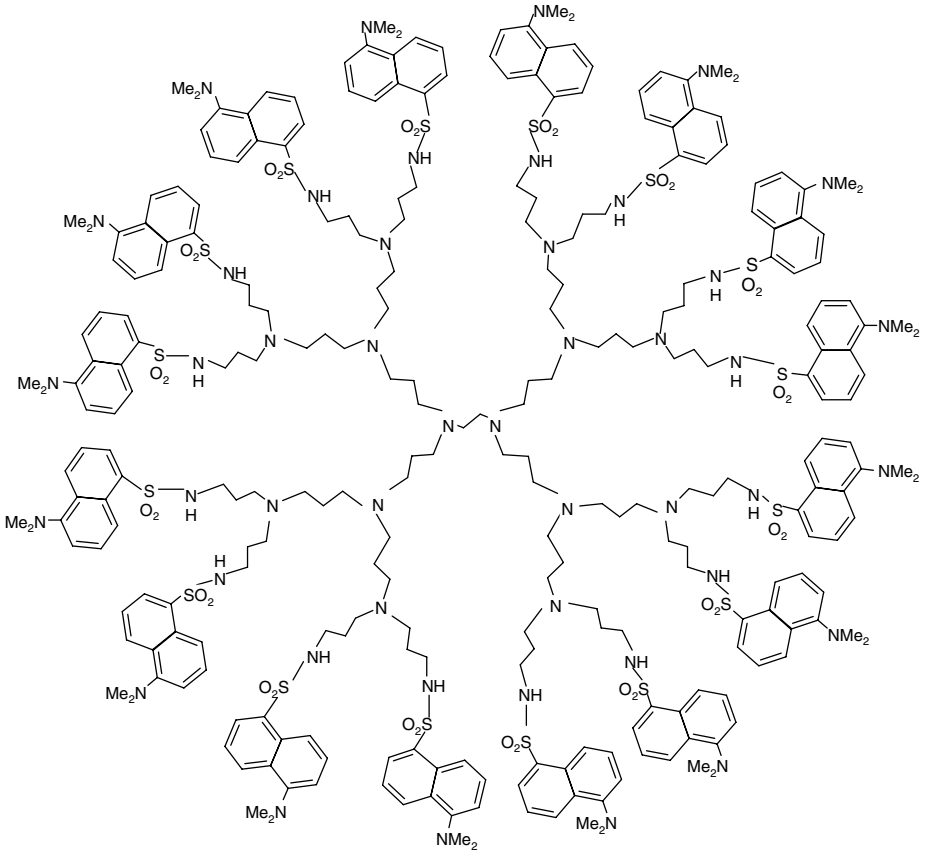

Fig. 1. Structural formula of third generation dansylated POPAM dendrimer (G3).

hosting by the POPAM used. Spectral changes related to complexation were monitored by absorption spectroscopy (Varian Cary 100 UV/vis) and by recording fluorescence spectra (Perkin–Elmer LS50B spectrometer).

Time-resolved measurements were done with a home built femtosecond transient absorption spectrometer. Seed pulses were provided by Ti-sapphire oscillator (Coherent MIRA 900) pumped with frequency doubled Nd:YVO_4 laser (Coherent Verdi 5W). Seed pulses were amplified in a multipass amplifier (Quantronix ODIN) pumped with a frequency doubled Nd:YLF laser (Quantronix). Amplified femtosecond pulses (800 nm, 800 μJ, 1 kHz) were directed to two home-built non-collinear optical parametric amplifiers (NOPA) that were used to tune the wavelength of pulses. UV-pulses were generated by sum frequency mixing of the output from NOPA, tuned to 588 nm, with fundamental frequency of 800 nm in a nonlinear crystal (BBO, 1 mm). Generated UV-pulses with center wavelength of 339 nm were used for excitation of the samples. In the kinetic measurements output from NOPA was used as a probe, while for transient spectra measurements white light continuum generated in a 2 mm sapphire plate with ~1 μJ of fundamental pulse energy was used. In all measurements polarizations were adjusted to magic angle by using a Berek polarization compensator (New Focus).

For UV excitation absorbance of the dansyl and eosin were adjusted to be approximately the same. For all dendrimer generations same optical density ca. 0.7 at the excitation wavelength was used. Under these conditions the G2 dendrimer had approximately one eosin, whereas the G3 dendrimer had two eosins and the G4 dendrimer four eosins per host.

3. Results

The absorption spectra of dansylated G3 POPAM in chloroform and eosin Y in ethanol are shown in Fig. 2. Other dendrimer generations show a similar shape of absorption spectra, absorption coefficient seems to depend only on the total number of dansyls per dendrimer. When eosin is associated with the dendrimer the absorbance of dansyls remains practically unchanged, but the absorption maximum of eosin shifts from 525 nm to 533 nm, a clear indication of non-covalent binding between eosin and the dendrimer. Fluorescence spectra of G3 POPAM and eosin solutions excited with 340 nm light are shown in the lower part of Fig. 2 together with the fluorescence spectrum of the dendrimer–eosin complex. When dansyls of the complex are selectively excited dansyl fluorescence is strongly quenched and slightly blue shifted, whereas red shifted fluorescence from the eosin becomes clearly observable. Fluorescence was always stronger in the eosin fluorescence region than in the dansyl fluorescence region independent of excitation wavelength.