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A dendrimer facilitates resonance energy transfer between hydrophobic aromatic guest molecules in water



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ABSTRACT

A water soluble third generation poly(alkyl aryl ether) dendrimer was examined for its ability to solubilize hydrophobic polyaromatic molecules in water and facilitate non-radiative resonance energy transfer between them. One to two orders of magnitude higher aqueous solubilities of pyrene (PY), perylene (PE), acridine yellow (AY) and acridine orange (AO) were observed in presence of a defined concentration of the dendrimer. A reduction in the quantum yield of the donor PY* emission and a partial decrease in lifetime of the donor excited state revealed the occurrence of energy transfer from dendrimer solubilized excited PY to ground state PE molecules, both present within a dendrimer. The energy transfer efficiency was estimated to be ~61%. A cascade resonance energy transfer in a three component system, PY*–to–PE–to–AY and PY*–to–PE–to–AO, was demonstrated through incorporation of AY or AO in the two-component PY–PE system. In the three-component system, excitation of PY resulted in emission from AY or AO via a cascade energy transfer process. Careful choice of dye molecules with good spectral overlap and the employment of dendrimer as the medium enabled us to expand absorption-emission wavelengths, from ~330 nm to ~600 nm in aqueous solution.

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1. Introduction

Nature that employs an efficient antenna system to absorb sunlight and perform photosynthetic reactions epitomizes the value of energy transfer processes that is useful to expand the wavelength between absorption and emission. Partial understanding of this phenomenon has led to the emergence of a repertoire of mimics of energy donors and acceptors, prompting development of several applications, such as, efficient opto–electronic devices [1–9]. The non-radiative fluorescence (Förster) resonance energy transfer (FRET) that plays a key role in photosynthesis involves energy transfer from an excited state donor to a ground state acceptor, through long-range dipole–dipole interaction [10,11]. The efficiency of such a process depends critically on the spatial orientation, distance between the donor and acceptor and spectral overlap between the donor emission and acceptor absorbance. In this context supramolecular assemblies, such as, zeolites [12], polymers [13–15], surfactants [16,17], vesicles [18], biomolecules

[19,20], macrocycles (resorcinarenes [21], cavitands [22] and cyclodextrins [23]) and clay materials [24–27] have been explored as a matrix to enable energy transfer between various donors and acceptors. FRET studies in aqueous solution are often hindered by near-insolubility of polycyclic aromatic donors and acceptor molecules. In the past this is overcome by the use of cyclodextrins and micelles that have the ability to solubilize water-insoluble guests in aqueous solution [28]. Several studies previously demonstrated that hyperbranched dendritic macromolecules, similar to cyclodextrins and micelles, can solubilize polycyclic aromatic molecules in water [29–38]. Presence of defined structural features and dynamic internal cavities of varying shapes and sizes is an advantage with dendritic macromolecules over micelles. We have recently established the value of a series of poly(alkyl aryl ether) dendrimers to encapsulate and fine-tune photochemical reactivities of hydrophobic guests in aqueous solution [29–32]. In the current investigation we have explored the utility of water-soluble dendrimers to bring about singlet–singlet energy transfer between aromatic molecules that are insoluble in water. The studies revealed that water-soluble poly(alkyl aryl ether) dendrimer can solubilize aromatic molecules pyrene (PY), perylene (PE), acridine orange (AO) and acridine yellow (AY) in basic aqueous solution and facilitate efficient Förster

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resonance energy transfer (FRET) between these molecules. Results of this study are presented below.

2. Experimental

2.1. Materials

Poly(alkyl aryl ether) dendrimer (**C5-G3**) was synthesized in the laboratory [39]. Chemicals, solvents and dyes were purchased from commercial sources. Dyes were used after further purification by crystallization. Deionized water from a Millipore Milli-Q Laboratory purification system was used for the experiments.

2.2. General protocol for encapsulation

PY or PE or AY or AO (1–2 mg) was mixed with a solution of **C5-G3** dendrimer (4.2 mg) in THF (2 mL), the solution evaporated in vacuo and dried. Aq. NaOH solution (10 mL) (pH ~9.5) was added to the resulting material, which provided a dendrimer concentration of 100 μM . The solution was sonicated for 5 min, stirred at room temperature for 12 h in dark, filtered through a 0.45 μm filter, absorption spectrum of the filtrate was recorded. Molar absorptivity values of aq. solutions (pH 9.5) were: PY $\epsilon_{335} = 50,603 \text{ M}^{-1} \text{ cm}^{-1}$; PE $\epsilon_{436} = 37,962 \text{ M}^{-1} \text{ cm}^{-1}$; AY $\epsilon_{436} = 24,083 \text{ M}^{-1} \text{ cm}^{-1}$; AO $\epsilon_{436} = 25,765 \text{ M}^{-1} \text{ cm}^{-1}$.

2.3. Optical studies

Steady-state absorption and emission measurements were performed at 25 °C on a UV–vis and fluorescence spectrophotometer, respectively. The slit width was 2 nm at both excitation and emission monochromators. Excitation and emission wavelengths for PY and PE solutions were 335 and 410 nm, and 373 and 446 nm, respectively. Titrations were performed by the addition of aq. dendrimer solution (1 mM) (25 μL), containing PE (59.2 μM) to an aq. dendrimer solution (5 μM) (4 mL), containing of PY (1.56 μM).

Experiments on the triad system were performed using aq. dendrimer solution (5 μM) (4 mL) (pH 9.5), containing PY (1.56 μM) to which the dendrimer solution (1 mM) (125 μL), containing PE (59.2 μM) was added. A dendrimer solution (100 μM) (50 μL), containing AY or AO (250 μM) was added further. Excitation wavelength was 335 nm. Control experiments of PY and AY or AO system, and PE and AY or AO system, both at 335 nm excitation wavelength, were performed. These experiments did not produce emission of the AY or AO.

Time resolved fluorescence studies were undertaken in a fluorescence lifetime spectrometer equipped with a thermostat. A light emitting diode at 335 nm with pulse width less than 1 ns was used as excitation source. Excitation and emission wavelength were read at 335 and 373 nm, respectively. Experiments were conducted by titration of an aq. dendrimer solution (200 μM) (25 μL) containing PE (11.8 μM) to the dendrimer solution (1 μM)

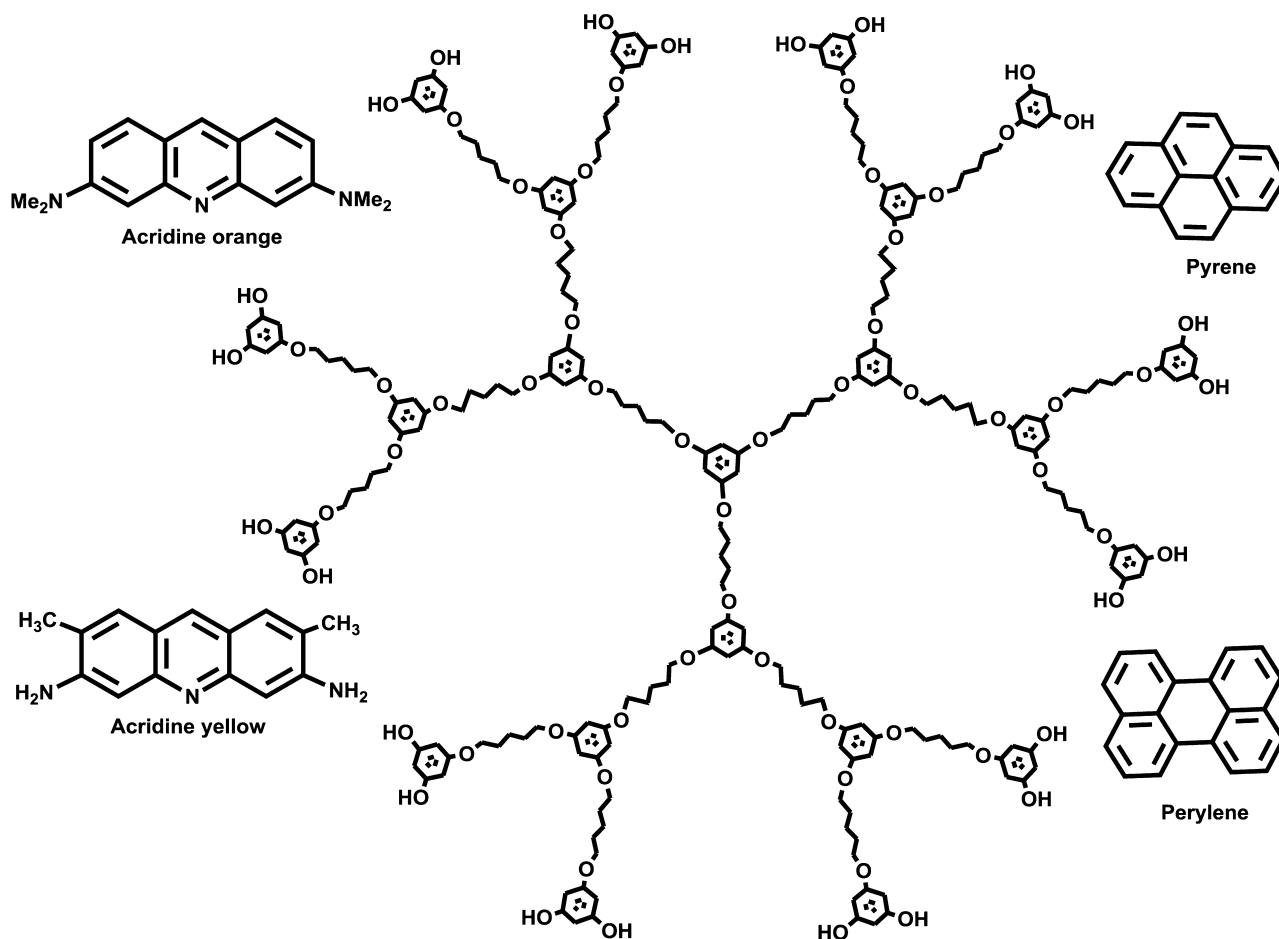


Fig. 1. Molecular structures of dendrimer host **C5-G3** and polyaromatic guest molecules.

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