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Förster resonance energy transfer between acridinediones and selected fluorophores—Medium dependence

R. Krishnaveni, P. Ramamurthy*

National Centre for Ultrafast Processes, University of Madras, Taramani Campus, Chennai-600113, India

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ABSTRACT

We report highly efficient Förster resonance energy transfer process between acridinedione dyes and basic fluorophores. FRET between free and β -cyclodextrin modified acridinediones as donors and fluorophoric dyes like safranin as acceptor were investigated in an alcoholic medium, polymer solution and a polymeric film. Efficiency of the processes were experimentally found by steady-state and time-resolved experiments for different donor and acceptor combinations. The associated spectral parameters viz., R^0 , $J(\lambda)$ were calculated, the Stern–Volmer relations based on fluorescence intensity and lifetime were constructed and the rates of energy transfer were calculated. The results indicated that the dominant mechanism responsible for the excitation energy transfer is that of resonance transfer due to long range dipole–dipole interaction and the process was found to be highly efficient when the medium was a constrained one as in the case of a polymeric film. A multifold enhancement in efficiency of energy transfer was also observed when the donor was a modified acridinedione when compared to a free acridinedione. The reason is attributed to the effective binding of the acceptor into the cavity of β -cyclodextrin.

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1. Introduction

Förster resonance energy transfer (FRET) is a process in which energy is transferred by a non-radiative, long-range dipole–dipole coupling from a fluorophore in an excited-state serving as a donor to another proximal ground state acceptor. FRET, a mechanism describing the non-radiative and distance-dependent energy transfer between two chromophores, is a powerful tool used in several fields of science. In physical chemistry and in biophysics, it is widely used in the study of a variety of biological phenomena, such as protein–protein and protein–DNA interactions, protein conformational changes, and other molecular dynamics [1]. Förster-type resonant energy transfer occurs between an excited donor and an acceptor molecule when their emission and absorption bands overlap sufficiently and their mutual distance is not much larger than the Förster radius (R^0). The latter is defined as the distance of a pair of donor and acceptor at which the FRET efficiency is 50%. Its precise value depends on the details of the donor–acceptor complex, such as dipole orientation factor and the spectral overlap between donor emission and acceptor absorption [2].

* Corresponding author. Tel.: +91 44 24547190; fax: +91 44 24546707.
E-mail addresses: prm60@hotmail.com,
perumal_ramamurthy@yahoo.co.in (P. Ramamurthy).

One of the fast emerging fields in current scenario is conjugated polymers (CPs) and molecular complexes (MCs), on account of the rapidly growing number of applications in which they are being used, including the development of transistors, flexible photovoltaic devices, light-emitting diodes, and optical biosensors. Among these fields of application, the latter is arguably one of the most promising [3]. Although progress in modern synthetic chemistry has led to synthesis of various well-defined CPs with optimized photophysical properties, many CPs offer insufficient photoluminescence and photostability and many supramolecules like cyclodextrins (CDs) are photochemically inactive. FRET donors when conjugated to such polymers and supramolecules enable the understanding of physical processes associated with such photo excited dyes which is important for the efficient conversion of optical energy to other spectral regions.

One such kind of photo excited dyes is the family of acridinediones which have been already established to possess good lasing properties. These kind of laser dyes are being currently widely used in spectroscopic systems for photophysical and photochemical studies, and energy transfer from such donor dyes to acceptor molecules has been found to have a pronounced effect on the operation and spectral output of the donor laser dyes [4]. It is the purpose of the present work to provide a new view of the phenomenon called as FRET to the acridinedione dyes. The acridinediones may have a promising future as more favorable donors in FRET based studies due to many reasons like—(i) a narrow

emission spectrum which would reduce the background signals and (ii) a high quantum yield, so that the efficiency of the process could be enhanced. The theory of energy transfer between unlike molecules due to resonance interaction in a condensed phase which has been formulated by Förster in a manner that is particularly acquiescent to experimental examination is followed in our current investigation.

The experimental verification of the Förster theory has been carried out under nanosecond and picosecond time scales by using various techniques [5]. According to Förster theory, the rate of energy transfer (k_{FRET}) [6] from a donor to an acceptor, separated by a distance ' r ' is given by,

$$k_{\text{FRET}} = \frac{1}{\tau_D^0} \left(\frac{R^0}{r} \right)^6 \quad (1)$$

where τ_D^0 is the lifetime of the donor in the absence of acceptor, R^0 is the Förster distance (Å) and ' r ' is the between the donor and acceptor. The Förster radius (R^0) is given by the Eq. (2)

$$R^0 = 0.211[\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6} \quad (2)$$

where Q_D is the quantum yield of the donor in the absence of acceptor [7], n is the refractive index of the medium, κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor. $J(\lambda)$ is the spectral overlap between donor emission and acceptor absorption and is given by Eq. (3) [8],

$$J(\lambda) = \frac{\int F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int F_D(\lambda) d\lambda} \quad (3)$$

where ' ε_A ' stands for the molar extinction co-efficient of the acceptor and the value of ' κ^2 ' may vary from 0 (mutually perpendicular transition dipoles) to 4 (collinear dipoles). For

random orientation of D and A dipoles, value of κ^2 is used as 2/3 for R^0 calculations [9].

The efficiency (E) of FRET process can be calculated from the steady-state and time resolved data as given by Eqs. (4) and (5).

$$E = 1 - \frac{I_{0D}}{I_D} \quad (4)$$

$$E = 1 - \frac{\tau_{0D}}{\tau_D} \quad (5)$$

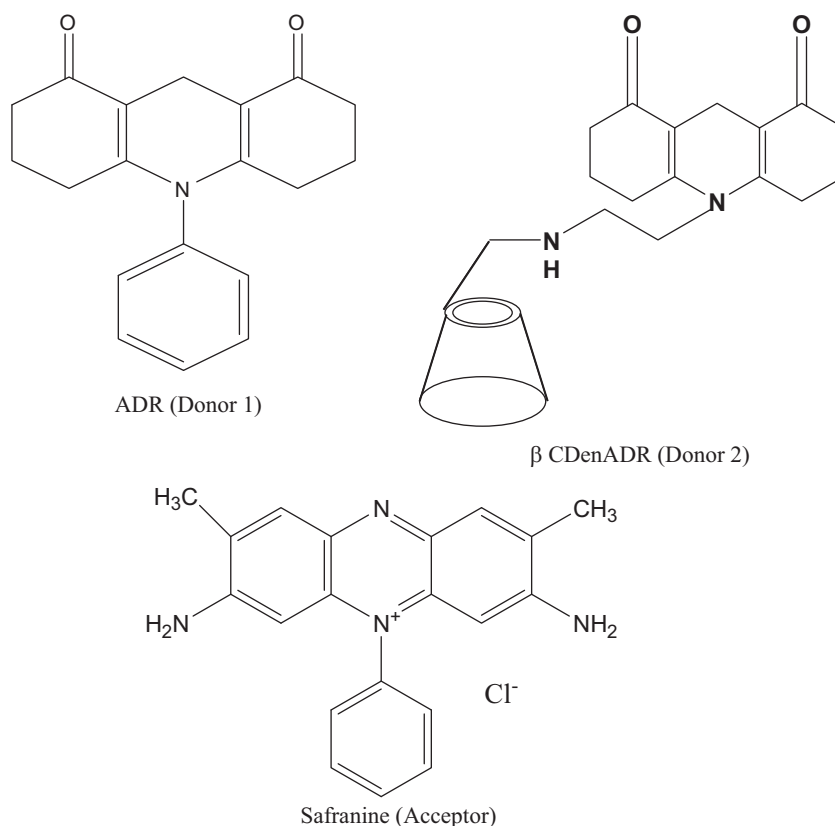
where I_{0D} , I_D , τ_{0D} , τ_D are the intensities and lifetimes of the donor in the absence and presence of acceptors, respectively [10].

Another area in which we have focused in the current study is the inclusion of fluorophores into the cavity of β -cyclodextrin which is a subject of great interest in recent years since it offers the so-called microenvironment in its nano cavities. Due to the limited space in the host cavity, dynamic effects may result due to geometric restrictions imposed on the host. Based on the unique molecular architecture of CD, various chromophore-modified CDs have been constructed and shown to act as molecular sensors or enzymes. So far reported, the chromophore-modified CDs acting as chemosensors have a single fluorophore or two identical fluorophores [11]. However, in this study, we have used a novel chromophoric cyclodextrin donor for FRET studies in which an acridinedione possessing two different chromophoric centres has been anchored to the cyclodextrin molecule.

2. Experimental methods

2.1. Chemicals used

Acridinedione (ADR) used was prepared in the laboratory following reported procedures [12]. Acridinedione modified



Scheme 1. Structures of donor and acceptor used in the studies.

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