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Fluorescence resonance energy transfer from pyrene nanoparticles to riboflavin: Spectroscopic insights and analytical application

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The aqueous suspension of fluorescent pyrene nanoparticles (PyNPs) have been prepared by a reprecipitation method in the presence of sodium dodecyl sulphate (SDS) as a stabilizer. The PyNPs shows bathochromically shifted aggregation induced enhanced emission in the spectral region 400 nm to 600 nm peaking at 466 nm where Riboflavin (RF) absorbs strongly. The systematic fluorescence resonance energy transfer (FRET) experiments performed by measuring fluorescence quenching of PyNPs with successive addition of RF analyte has exploited the use of PyNPs as nano probe for detection of RF in aqueous solution with lower limit of detection 10.163×10^{-5} mol.L^{-1}. The fluorescence of PyNPs is quenched by RF and quenching is in accordance with the Stern-Volmer relation. The distance r between the donor (PyNPs) and acceptor (RF) molecules has been obtained according to the FRET method. The evaluation of photo kinetic and thermodynamic parameters such as quenching rate constant (k_q), enthalpy change (ΔH), Gibbs free energy change (ΔG) and entropy change (ΔS) are calculated by quenching results obtained at different constant temperatures. The proposed FRET method based on fluorescence quenching of PyNPs is used further to develop an analytical relation for estimation of RF from pharmaceutical samples available commercially in the market.

Keywords Fluorescent pyrene nanoparticles, Riboflavin, Fluorescence resonance energy transfer

Riboflavin (7, 8-dimethyl-10-ribityl-isoalloxazine) also known as vitamin B_2 is a yellow fluorescent dye, unique among the water soluble vitamins and present in a wide variety of foods. It was firstly isolated from milk and given the name lactochrome. It can be crystallized as orange-yellow crystals[1,2]. This vitamin is an essential component of two major coenzymes flavin adenine mononucleotide (FMN, also known as riboflavin-5'-phosphate), and flavin adenine dinucleotide (FAD). These coenzymes play major roles in energy production, cellular function, growth, and development, and metabolism of fats, drugs, and steroids[3-5]. Various modern investigations strongly recommend that RF has tremendous potential to be used in improving the chemotherapeutic potential of major anticancer drugs[6]. It is very stable during thermal processing, storage and food preparation. It cannot be synthesized in the human body; therefore it must be obtained from dietary sources such as liver, cheese, milk, meat, eggs, wine and tea. Thus, consumption of vitamin B_2 depleted food can result in health problem. RF and related compounds are necessary for cell growth and development. On the other hand, its concentration in blood must be controlled while most of it is excreted through urine.[7–9]. The absorption spectrum of RF shows two bands peaking at 372 nm and 445 nm and is known for its characteristic fluorescence[10].

Fluorescence resonance energy transfer (FRET) is a non-radiative process whereby an excited state donor (D) transfers energy to a ground state acceptor (A). The donor and acceptor molecules are coupled by a dipole-dipole interaction. There is no intermediate photon in FRET, and it mainly occurs over distances comparable to most biological macromolecules, i.e., about 10–100 Å[2,11-12]. Organic probes based on fluorescence quenching approach are widely used for detection and sensing of molecules of physicochemical, biological and environmental concern[13-14]. Perylene, anthracene and pyrene are the most extensively used probes in micellar medium because of their high fluorescence quantum efficiency to sense biomolecules[15], pharmaceutical samples[16], dyes[17], and metal ions[18]. On the other hand, the use of aggregation-induced enhanced emission of nanoparticle suspension is of current research interest[19,20]. The technique of analysis