

## Sensing Study through Resonance Energy and Electron Transfer between Förster Resonance Energy Transfer Pair of Fluorescent Copolymers and Nitro-Compounds

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**Abstract :** Förster Resonance Energy Transfer (FRET) is a powerful technique used to probe close-range molecular interactions. Physically, the FRET phenomenon manifests as a dipole-dipole interaction between closely juxtaposed fluorescent molecules (10-100 Å). Our effort is to employ this FRET technique to make a prototype device for highly sensitive detection of environment pollutant. Among the most common environmental pollutants, nitroaromatic compounds (NACs) are of particular interest because of their durability and toxicity. That's why, sensitive and selective detection of small amounts of nitroaromatic explosives, in particular, 2,4,6-trinitrophenol (TNP), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) has been a critical challenge due to the increasing threat of explosive-based terrorism and the need of environmental monitoring of drinking and waste water. In addition, the excessive utilization of TNP in several other areas such as burn ointment, pesticides, glass and the leather industry resulted in environmental accumulation, and is eventually contaminating the soil and aquatic systems. To the date, high number of elegant methods, including fluorimetry, gas chromatography, mass, ion-mobility and Raman spectrometry have been successfully applied for explosive detection. Among these efforts, fluorescence-quenching methods based on the mechanism of FRET show good assembly flexibility, high selectivity and sensitivity. Here, we report a FRET-based sensor system for the highly selective detection of NACs, such as TNP, DNT and TNT. The sensor system is composed of a copolymer Poly [(N,N-dimethylacrylamide)-co-(Boc-Trp-EMA)] (RP) bearing tryptophan derivative in the side chain as donor and dansyl tagged copolymer P(MMA-co-Dansyl-Ala-HEMA) (DCP) as an acceptor. Initially, the inherent fluorescence of RP copolymer is quenched by non-radiative energy transfer to DCP which only happens once the two molecules are within Förster critical distance ( $R_0$ ). The excellent spectral overlap ( $J\lambda = 6.08 \times 10^{14} \text{ nm}^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) between donors' (RP) emission profile and acceptors' (DCP) absorption profile makes them an exciting and efficient FRET pair i.e. further confirmed by the high rate of energy transfer from RP to DCP i.e.  $0.87 \text{ ns}^{-1}$  and lifetime measurement by time correlated single photon counting (TCSPC) to validate the 64% FRET efficiency. This FRET pair exhibited a specific fluorescence response to NACs such as DNT, TNT and TNP with 5.4, 2.3 and 0.4  $\mu\text{M}$  LODs, respectively. The detection of NACs occurs with high sensitivity by photoluminescence quenching of FRET signal induced by photo-induced electron transfer (PET) from electron-rich FRET pair to electron-deficient NAC molecules. The estimated stern-volmer constant (KSV) values for DNT, TNT and TNP are  $6.9 \times 10^3$ ,  $7.0 \times 10^3$  and  $1.6 \times 10^4 \text{ M}^{-1}$ , respectively. The mechanistic details of molecular interactions are established by time-resolved fluorescence, steady-state fluorescence and absorption spectroscopy confirmed that the sensing process is of mixed type, i.e. both dynamic and static quenching as lifetime of FRET system (0.73 ns) is reduced to 0.55, 0.57 and 0.61 ns DNT, TNT and TNP, respectively. In summary, the simplicity and sensitivity of this novel FRET sensor opens up the possibility of designing optical sensor of various NACs in one single platform for developing multimodal sensor for environmental monitoring and future field based study.

**Keywords :** FRET, nitroaromatic, stern-Volmer constant, tryptophan and dansyl tagged copolymer

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