# A Time-Resolved Area Normalized Emission Spectral Investigation of Excited-State Proton Transfer Dynamics in Micellar-Polycationic Molecular Interface: A Model Drug Delivery- Drug Sequestration Approach

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Excited-state proton transfer dynamics is a well-known tool to probe confined assembly sites selectively, which provides the nature of the local microenvironment, hydration nature, local rigidity, lability of water molecules in the confined space.[1] These are not only the properties that provide us with the nature of the assembly, but we can also assess the biological system having such similar properties. Proton transfer is a fundamental chemical reaction that governs many biochemical processes in living bodies and many energy harvesting systems. In our present scenario, we may have to encounter lots of systems comprising of excited-state dynamics to be in a functional state in a biomolecular system.[2] These biological environments often contain polyionic molecules like DNA, RNA, protein, etc. So, the presence of both micellar assembly and polyionic molecules may alter the dynamical nature of the probe. Polyelectrolyte molecules are well known for coacervate formation, multilayer thin-film formation having wide applications in biological to industrial sectors.[3] Polyelectrolytes of opposite charges form a mixed aggregate that may function as membrane less organelle and can be biomimicking. Small ionic chain surfactants also form mixed aggregates of different kinds based on the charge properties. The polycationic electrolyte PDADMAC also forms macromolecular aggregate with anionic surfactant, polyanionic electrolytes, etc. But the nature of interaction among cationic or zwitterionic surfactant with cationic polyelectrolyte PDADMAC is not studied in details.

In our present investigation, we have incorporated the photoacid probe HPTS in the micellar- polycationic PDADMAC interface to explore the nature of interaction among the probe, micellar assembly, and the polycationic molecules. Again, we have rigorously investigated how these interactions modulate the excited-state proton transfer dynamics based on the time-resolved area normalized emission spectra and the nature of isoemissive point shifts. The shuttling of the probe between the micellar assembly and the polycationic molecule also convinces us to take it as a drug delivery- drug sequestration approach depending on the micellar assembly's nature.

We have explored the detailed steady-state fluorescence emission spectra of HPTS and time-resolved emission of HPTS and MPTS, along with the time-resolved anisotropy decay in the polycationic PDADMAC- micellar interface. Apart from that, we have carried out a dynamic light scattering study of the mixed molecular assembly both in the presence and absence of the probe molecule. The constructed overlap corrected time-resolved area normalized emission spectra of HPTS have more than one isoemissive point, which substantiates the evidence that in the polycationic micellar interface, more than one equilibrium process is going on based on different locations of the probe's attachment. So, on the course of concentration variation of PDADMAC, the probe migrates one site to another as per the microenvironment orchestrated by the assembly.

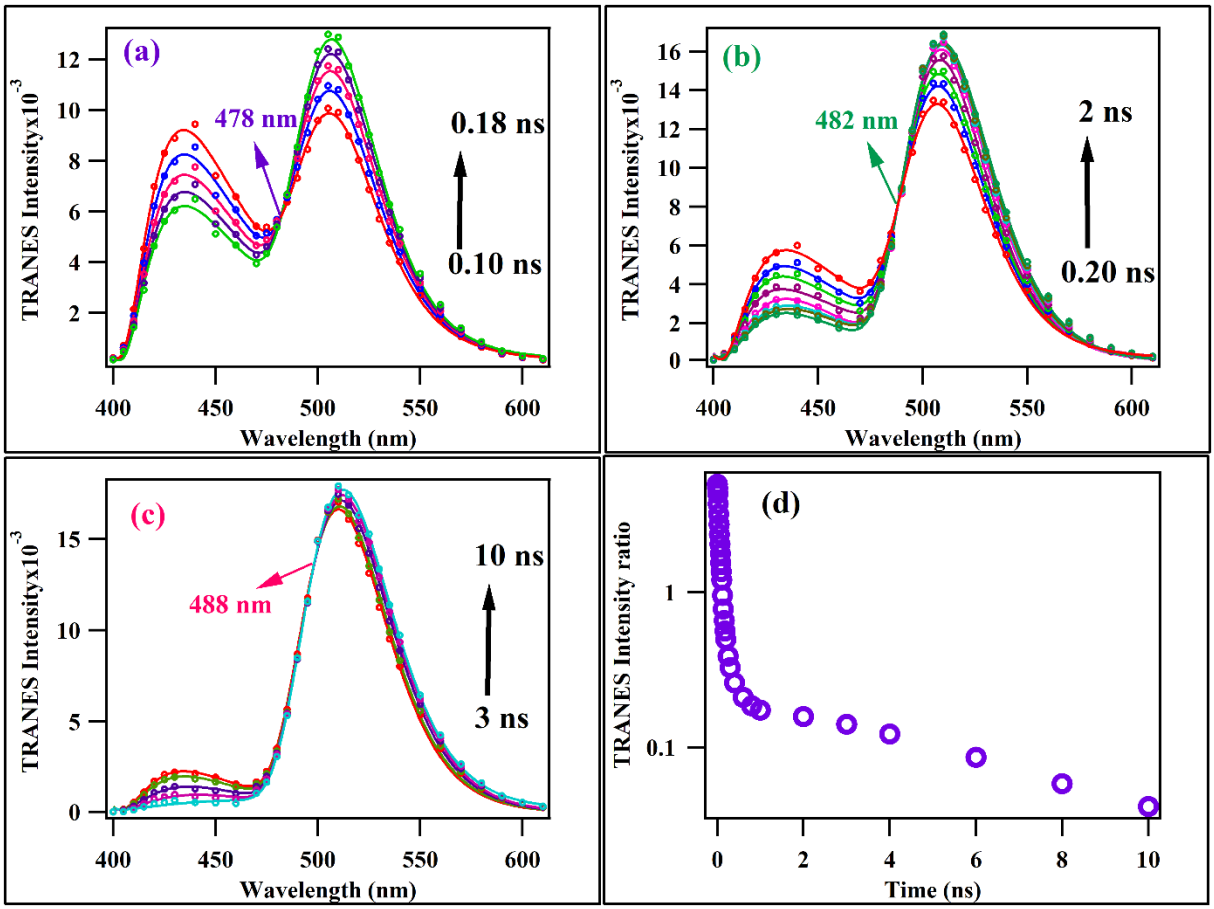


**Figure 1:** TRANES profile of HPTS in micellar SB12- 0.084 µM PDADMAC with different time zone (a) 0.10 ns to 0.18 ns (b) 0.2 ns to 2 ns (c) 3 ns to 10 ns with three isoemissive points and (d) TRANES emission intensity ratio of protonated/deprotonated (ROH/RO) with the variation of times.

In the DLS study, we have observed that the micellar structure remained intact, and also, there is no probe-induced polycationic molecule aggregation. From TRANES, we obtained isoemissive point shift on certain time zone while varying PDADMAC concentration which provides us the migration of the probe from one micellar interface to the polycationic molecule, which can be utilized as the drug delivery-sequestration phenomena, also this system can be applied in industrial dye removal purpose from wastewater.

## References

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