



Rapid Communication

Unconventional Modulation of Fluorescence Anisotropy of 3-Hydroxyflavone in Cationic Micelles

Sinjan Das, Nitin Chattopadhyay*

Department of Chemistry, Jadavpur University, Kolkata 700 032, India



ARTICLE INFO

Article history:

Received 17 October 2016

Received in revised form 12 November 2016

Accepted 4 December 2016

Available online xxxx

Keywords:

3-Hydroxyflavone

Fluorescence anisotropy

ESIPT

CMC

Solvated structure

Hydrogen bonding

ABSTRACT

Atypical trend for the fluorescence anisotropy of an excited state intramolecular proton transfer (ESIPT) prone molecular system, namely, 3-hydroxyflavone (3HF) has been reported in the aqueous cationic micellar media. Contrary to the conventional rising trend of fluorescence anisotropy for fluorophores with the addition of the micellar environments, 3HF exhibits a decreasing trend in the fluorescence anisotropy in cationic micelles. Disruption of the intermolecular hydrogen bond induced solvated structure involving 3HF and the water molecules is assigned to be responsible for this unusual modulation of the fluorescence anisotropy in the micellar microenvironments. As micelles mimic the bio-membranes, this unconventional behavior of the fluorescence anisotropy of 3HF is significant to understand the intricacies of solvation and thereby action of bioactive ESIPT prone flavonoid molecules in bio or biomimicking environments.

© 2016 Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Study of different photophysical aspects of the excited state intramolecular proton transfer (ESIPT) prone molecular systems in both homogeneous and heterogeneous environments has been a prime arena of research since long because of their biological applications as well as their applicability as useful organic light sources covering a wide range in the visible region [1,2]. Flavonoids, abundant in the vegetal kingdom, are the important members of this category that also act as potential antioxidants [3]. 3-Hydroxyflavone (3HF) (Scheme 1) is the simplest molecular system of the bioactive flavonoid family and it is one of the most extensively studied ESIPT probes in both homogenous and microheterogeneous environments pioneered by Sengupta and Kasha, later on followed by other research groups [4–14]. Surprisingly, in spite of a large number of reports on different photophysical aspects of 3HF and other flavonoids, one of the fundamental parameters, namely the fluorescence anisotropy, has remained unexplored. In one of our recent articles, we have demonstrated for the first time that the fluorescence anisotropies of the ESIPT prone flavonoids in protic solvents are unusually high compared to the situations for other fluorophores, in general, in similar solvents [15]. On the contrary, in less polar solvents (like chloroform, heptane etc.), the fluorescence anisotropies of the studied flavonoids are found to be very low. These are indicative of the interaction of the probe with the solvents, in particular, the protic ones. Time resolved fluorescence anisotropy measurements reveal that the rotational motion of 3HF is substantially constrained in protic media, especially in water. Based on the observations, we have

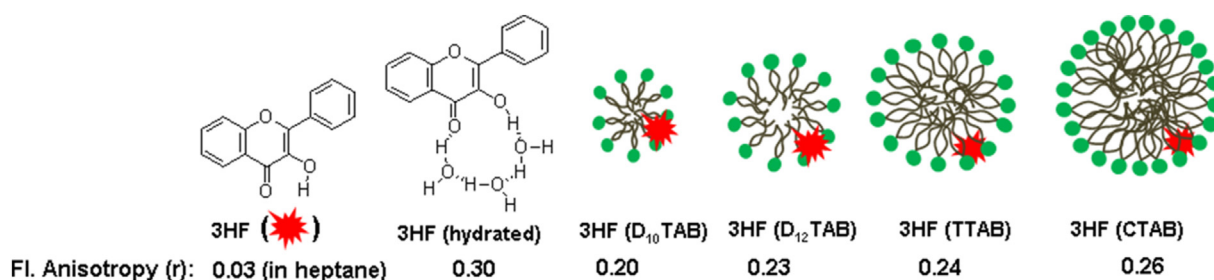
proposed the formation of intermolecular hydrogen bond induced cage-like structure involving the probe and the protic solvent molecules resulting in an increase in the effective volume of the probe, which is responsible for such high fluorescence anisotropies in protic media [15].

Fluorescence anisotropy is often exploited as a key tool to unravel the rotational intricacies of a probe in microheterogeneous environments. In common solvents, the fluorophores rotate very fast within their fluorescence lifetimes, giving rise to very low (close to zero) fluorescence anisotropy [16]. Different factors perturbing the flexibility of a randomly rotating probe like association of the probe in organized or macromolecular systems affect the observed fluorescence anisotropy [16]. The enhanced effective size of the probe and the rigidity of the immediate environment around the probe make the rotational motion considerably slow resulting in a high fluorescence anisotropy of the bound probe [5,8,9,12,13,17–21]. Thus upon gradual addition of such microheterogeneous media, the fluorescence anisotropy of the probe generally reveals an increasing trend until a saturation value is achieved. Contrary to the commonly observed increasing trend in the fluorescence anisotropy values of fluorophores with the addition of the microheterogeneous environments, interestingly, we have observed an atypical decreasing trend in the fluorescence anisotropy of 3HF in motionally restricted cationic micellar environments. Additionally, as a useful byproduct of our study, we have demonstrated that the steady state fluorescence anisotropy of 3HF can be exploited to determine the critical micelle concentrations (CMCs) of the micelles.

Unprecedented high fluorescence anisotropy (~0.30) of the normal emission (~410 nm) of 3HF in protic solvents and very low anisotropy (~0.03) of the same in aprotic solvents like chloroform, heptane etc.

* Corresponding author.

E-mail address: nitin.chattopadhyay@yahoo.com (N. Chattopadhyay).



Scheme 1. Schematic structures of 3HF, hydrated 3HF and 3HF bound to the different nTAB micelles with the fluorescence anisotropy values of the corresponding species.

have prompted us to investigate its modulation in micellar environments. It is pertinent to mention here that the photoproducted tautomer (~510 nm) of 3HF reveals low fluorescence anisotropy values

irrespective of the proticity and polarity of the solvents [15] and exhibits the usual increasing trend of the same in restricted microheterogeneous media [5,8,9,11,12]. Contrary to the fluorescence anisotropies of most of

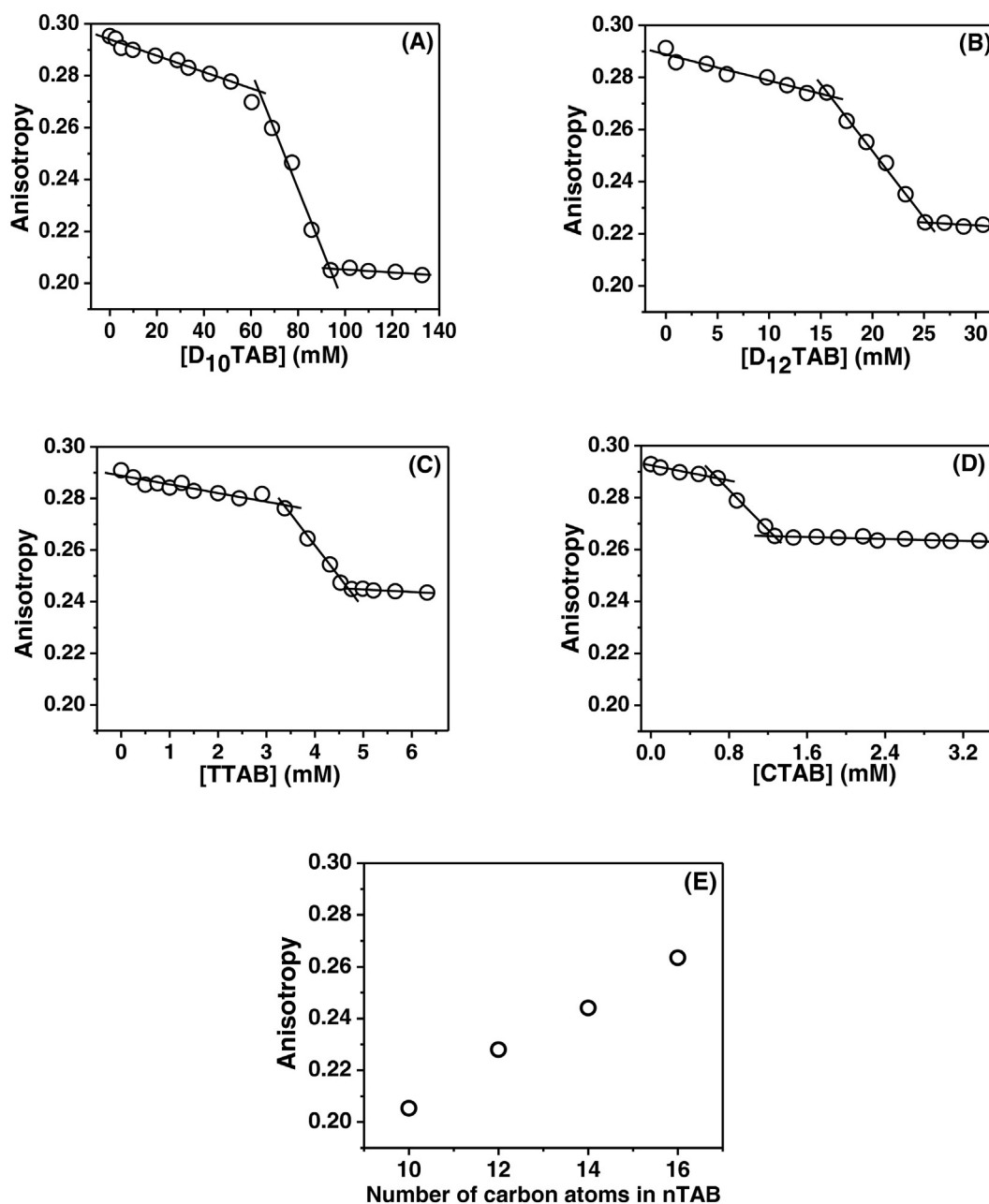


Fig. 1. Variation of the fluorescence anisotropy of 3HF with varying concentrations of (A) D₁₀TAB, (B) D₁₂TAB, (C) TTAB (D) CTAB. Variation of the same at the saturation level as a function of number of carbon atoms in the alkyl chain of the nTAB surfactants is presented in (E). $\lambda_{\text{ex}} = 345$ nm and $\lambda_{\text{monitored}} = 410$ nm. [3HF] ≈ 10 μM . Anisotropy values at each concentration of nTABs are averaged over 15 individual and consistent measurements.

Download English Version:

<https://daneshyari.com/en/article/4981573>

Download Persian Version:

<https://daneshyari.com/article/4981573>

[Daneshyari.com](https://daneshyari.com)