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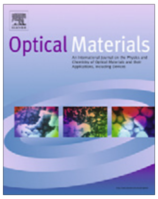

Spectral properties of 3-hydroxyflavone embedded in polysiloxane: Effects of the polymerization method

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ABSTRACT

The optical properties of 3-hydroxyflavone (3HF) embedded in siloxane matrices obtained through different synthetic procedures are herein presented for the first time. In this work, polysiloxanes derived from Room Temperature Vulcanization (RTV) by (i) Pt catalyzed hydrosilylation, (ii) tin catalyzed polycondensation and (iii) moisture induced polycondensation are loaded with 3HF molecule both by direct dissolution of 3HF within the siloxane precursors and by swelling of the bare siloxanes from 3HF acetone solutions. The structural changes of the 3HF molecule as the cross-linking reaction proceeds are monitored by FT-IR spectroscopy, whereas the evolution of the optical features of the dye molecule and in particular of the Excited State Intramolecular Proton Transfer (ESIPT) mechanism in the course of RTV is observed by fluorescence and excitation spectroscopy.

1. Introduction

The development of materials for conversion of UV light to higher wavelengths, i.e. to lower energies, is a key task in many applications. Luminescent down converters (LDCs) or luminescent solar concentrators (LSCs) are based on wavelength shifting (WLS) dye molecules or quantum dots, aiming to convert part of the solar spectrum into suitable wavelengths for high efficiency solar cells [1,2]. Among the WLS compounds, 3-hydroxyflavone (3HF) is one of the most studied, owing to its unique properties: the well known Excited State Intramolecular Proton Transfer (ESIPT) mechanism in 3HF enables emission in the green region upon excitation in the UV range. The high Stokes shift of the tautomeric form (about 180 nm) hinders re-absorption [3–5], thus leading to a widespread use of 3HF as fluorescent probe in several applications.

Though the dual fluorescence behavior of 3HF was explained through ESIPT mechanism in the late 1979 by Sengupta and Kasha [3], the study of ESIPT is still a lively topic of research, owing to the influence on the rate of proton transfer at the excited state of several parameters such as medium viscosity and temperature [6], environment polarity and hydrogen bonding capabilities [7]. More recent theoretical investigations, involving quantum chemical calculations to elucidate the nature of both the ESIPT mechanism and the ground state reverse proton transfer mechanism (GSRPT) [8], or time-resolved fluorescence studies related to intramolecular proton transfer (IPT) from the highest singlet states in 3-hydroxyflavone [9] have been carried out and further elucidated the kinetics of these different excitation/de-excitation pathways.

Since 3HF molecule can assume different forms that can prevail under specific conditions, its use to optically probe the local microenvironment has been thoroughly exploited. Many studies related to this dye embedded in different environments such as in alcoholic media [7,10], DMSO, cyclohexane [11], supercritical fluids [12] have been performed. As fluorescent protein probe, 3HF was used in a optical system where excited state Forster energy transfer from tryptophan (donor) is coupled with intramolecular proton transfer of 3HF (acceptor) [13]. 3HF has been also deposited by physical vapour deposition as pure compound and optical properties of the thin film have been related to possible structure changes during the plasma process [14].

Still another object of great interest is the class of 3HF derivatives, with special focus on their use as fluorescent probes in biomedical research, where functionalization of the parent 3HF and 3-hydroxychromone molecules is performed with the double aim of increasing affinity with the biomolecules to be sensed and improving solvatochromism through dye-environment interactions enhancement [15,16].

Metal ions complexation capabilities of 3HF and derivatives, such as morin, quercetin and other substituted flavonoids, have been also exploited in the field of chemosensing: several complexes ([17–20] and references therein), have been studied in relation to the effect of metal chelation on the fluorescence features, antioxidative properties, cytotoxicity and photodegradation rate of the free ligand, either 3HF or derivatives.

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Complexes of 3HF with Al(III), Zn(II) and Pb(II) have been used as model compounds to study photoinduced decomposition reactions occurring in soil organic matter in presence of potentially toxic metal cations [21]. Fluorimetric titration of Zn(II) complexes of 3HF allowed the determination of trace levels of metal cation [22], whereas metal ion complexation (Sb, Bi, Mo) assay for the specific quantitative determination of 3-hydroxy-substituted flavonoids has been assessed by Viswanathan and co-workers [23]. Flavonoid–metal complexes aid in the treatment of non-curable diseases has been studied by several research groups and promising data have been collected [24].

Though the entrapment of 3HF in suitable solid media can be very challenging, owing to 3HF sensitivity to polarity and hydrogen bonding of the medium, several authors performed the synthesis of 3HF-containing hybrid materials and studied with particular interest the preservation of the dye optical properties. 3HF has been entrapped in sol–gel derived matrices by direct dissolution in the sol [6,25] or by post-doping of dried xerogels through impregnation [26].

Emission from 3HF has been exploited in designing polymer based radiation resistant scintillator detectors [27,28], where the high Stokes shift of the dye dissolved in polystyrene or polyvinyltoluene encompasses the simultaneous role of primary dye and of waveshifter. Fabrication by plasma assisted chemical vapour deposition of 3HF-containing thin films has been performed to implement devices such as UV sensors, UV-to-visible wavelength shifters, and UV filters [29].

3-Hydroxyflavone undergoes acid-base equilibria, affording ionic species: the neutral form shows absorption at about 350 nm and emission from the normal excited state (N^*) at 400 nm and at 530 nm from the tautomer (T^*) in anhydrous dimethylsulfoxide (DMSO) upon excitation at 345 nm [30]; the anionic form is reported to display absorption in the range 400–450 nm and emission at about 480 nm in alcoholic media [10]. However, more recent studies on the influence of solvents with different hydrogen bonding accepting/donating capabilities proved that a wide range of absorption and emission wavelengths is covered by 3HF anion [30], to such an extent that the anion itself can be efficiently used to optically probe the chemical nature of the environing medium.

Besides the acid-base sensitivity, optical features of 3HF are strongly affected by the medium properties, which affect the ESIPT mechanism (Fig. 1). In the case of polar media, with hydrogen bonding capabilities, the intramolecular proton transfer can be remarkably hindered, thus leading to enhanced emission in the violet region from N^*. The tautomeric form, which emits at longer wavelengths, is most suitable for applications demanding large Stokes shift, as in the case of solar applications. The emission from this form is enhanced in case of apolar, aprotic solvents. The tautomeric form presents absorption at 350 nm and emission at 530 nm. In this case, the large Stokes shift (180 nm) minimizes re-absorption phenomena.

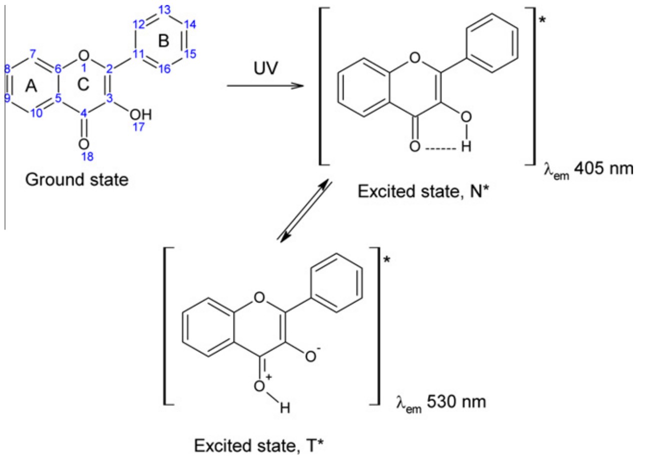

Fig. 1. ESIPT mechanism in 3HF molecule. Atoms numbering and ring labels are provided for 3HF at the ground state.

In this paper the entrapment of 3HF in polysiloxane is explored. Polysiloxanes present good heat resistance, rubber-like nature, waterproofness, biocompatibility and very low glass transition temperature. Moreover, polysiloxane is characterized by high transparency, low refractive index and high photostability, so that it is considered a suitable medium for solar applications.

Polysiloxanes are made by a backbone of Si—O—Si chains surrounded by side substituents such as hydrogen, methyl, phenyl, alcoholic groups, affecting the general properties of the whole matrix. Different types of chemical reactions are possible to obtain cross-linked polysiloxanes. In this paper poly-addition and polycondensation are used.

In this work, three types of phenyl-containing polysiloxanes have been tested in the aim to select the best matrix to host 3-hydroxyflavone. The phenyl substituents are chosen to enhance the compatibility with 3HF, in terms of solubility and refractive index, thus optimizing optical match with solar cells [31].

2. Experimental

3HF was bought from Sigma Aldrich (purity ⩾98%) and used as received. The components of the siloxane resins were purchased from ABCR GmbH; their structures are reported in Fig. 2. The dye was used in two ways: (a) the dye was directly dissolved in the base siloxane resin (concentration varies from 0.1% to 2%) and kept under stirring at 50° overnight; (b) a 0.1 M solution of dye in acetone (Sigma Aldrich, laboratory grade, purity ⩾99.5%) was used to induce swelling of the polysiloxane matrix: the sample was drowned into the solution, left for 3 days, dried under mild conditions at room temperature for 8 days with slow removal of solvent to avoid differential shrinkage of surface versus core.

Three different types of polysiloxane resin were chosen as matrices for embedding 3HF. The first one (labelled as PtCAT) is produced by polyaddition of vinyl terminated diphenyl–dimethyl–siloxane copolymer (A) (22–25 mol% of diphenyl groups, viscosity 1000–1500 cSt) and methylhydrosiloxane–phenylmethylsiloxane copolymer, hydride terminated (B) (45–50 mol% of phenyl groups, viscosity 75–110 cSt), catalyzed by Pt divinyltetramethyldisiloxane complex in xylene (Pt content 2.1–2.4%).

The second one (labelled as SnCAT) results from two-step polycondensation of silanol terminated diphenyl–dimethyl siloxane (C) (14–18 mol% of diphenyl groups, viscosity 50–60 cSt) and poly(diethoxysiloxane) (D), catalyzed by dibutyltin dilaurate (DBTDL).

The third system (labelled as ACET) is based on moisture induced polycondensation without catalyst, involving a reaction between silanol terminated diphenyl–dimethyl siloxane (C) (14–18 mol% of diphenyl groups) and methyltriacetoxysilane (E) (purity 95%).

For each system, several experimental trials were performed in order to find the best proportion between components to obtain transparent, bubbles free, non-sticky objects, which can be easily formed by casting in polyethylene vessels and extracted without tear.

Excitation, fluorescence and absorption spectra were collected from both solid and liquid solutions of each component.

UV–visible absorption measurements were performed with a Jasco V-570 dual-beam spectrophotometer in transmission mode. Fluorescence emission and excitation spectra at room temperature were collected by a Jasco FP-770 spectrofluorimeter equipped with a 150-W xenon lamp in front face geometry.