

Fluorescence and photochemistry of flavonols. A combined spectroscopic and Car-Parrinello study

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Flavonols are naturally-occurring molecules with interesting biological properties. They also have a peculiar photochemical behavior: when excited, their fluorescence spectrum is very sensitive to the surrounding environment. This behavior relies mainly on an excited-state intramolecular proton transfer (ESIPT) producing a (usually green) fluorescent tautomeric form of the molecule. Under some conditions, this ESIPT is partially or totally hampered, so that (usually violet) fluorescence from the normal state occur. Other phenomena, like ground-state deprotonation of OH groups, also strongly modify fluorescent properties [1].

Several synthetic flavonols (and 3-hydroxychromone derivatives) have been developed and are currently used as environment-sensitive fluorophors in biomedical research [1,2]. Similarly, natural flavonols (e.g. quercetin) are used as endogenous fluorophors in biochemistry [1].

We have investigated by electronic (UV-Vis, fluorescence, flash photolysis) and vibrational spectroscopies (Raman, Resonance Raman) the excited-state and ground-state proton transfer of several flavonols, including 3-hydroxyflavone and quercetin [3, 4]. Spectroscopic data obtained in several solvents have been interpreted through quantum chemical calculations (TD-DFT), whereas Car-Parrinello molecular dynamics (CPMD) made it possible to visualize processes like hydrogen bond formation and disruption (Seitsonen et al, in preparation).

A peculiar attention has been paid on the effect of the solvent-induced deprotonation of OH groups, not only to rationalize modification of fluorescence and other spectroscopic properties, but also in the chemistry (e.g. reactivity toward oxidative species [5]) and photochemistry of flavonols [6 and refs. therein].

For quercetin, deprotonation of OH group(s) was found to be the key parameter in transforming a weakly fluorescent neutral molecule to strongly emitting mono-, di-, tri-anionic species [3]. This aspect is particularly relevant in order to interpret quercetin fluorescence data in biochemical studies [1].

The investigation has been also extended to other flavonoids (flavone, luteolin, chrysin, apigenin, 7-hydroxyflavone, 5-hydroxyflavone).

The results will be discussed in the framework of the use of flavonols and 3-hydroxychromone derivatives as environment-sensitive fluorophors, as well as of their photochemistry and of their reactivity towards reactive oxidative species.

References

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