A relation between the tunable solvatochromism of D-π-A dyes and their ionicity. The case of pentacyanoferrate(II) bipyridine complexes.

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Solvatochromism is an important chromic phenomenon a compound can exhibit corresponding to the change of color upon alteration of the polarity of the medium in which this compound is dissolved.[1] The most characteristic class of solvatochromic dyes is that of organic dyes with structure of the type: "D-π-A" which corresponds to a system possessing an electron donating group (D) and an electron withdrawing group (A) separated by a π-conjugated system (π), aromatic in many cases. Such dyes have been extensively studied the last few decades, and their use in high-tech applications is currently being investigated by many research groups, involved in disciplines such as chemical synthesis, molecular electronics, materials science and technology, *etc*.[2]

Controlling the intensity of solvatochromism of a D-π-A dye is very important as this can lead to systems which allow human control, and which could be used as molecular switches and sensors of medium polarity with a vast number of applications. The main feature which drastically affects the intensity of the solvatochromism of a compound is the degree of ionicity this compound exhibits in a certain medium, corresponding in case of D-π-A dyes to the degree of charge transfer from D to A through π.[3]

We have recently shown that the degree of ionicity of pentacyanoferrate(II) complexes bearing bipyridine segments, is tunable in glucose solutions and that could possibly allow for sensing of glucose concentration in aqueous solutions.[4]

Herein, we report on a new way to determine the degree of ionicity of a D-π-A solvatochromic dye in media of different polarity. While Saito *et al.* have proposed such a method based on an empirical solvent polarity scale: the so-called Reichardt scale [$E_T(30)$],[1, 3] our approach is based mainly on dipolarity of solvents and the model of Suppan and Tsiamis.[5] This method is applied in case of pentacyanoferrate(II) dyes, synthesized by our research group and the results are compared to the results of the method of Saito *et al*.

References:

[1] C. Reichardt, *Chem. Rev. 94* (1994) 2319.

[2] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, third edn., Wiley-VCH, 2003.

[3] G. Saito et al., *J. Am. Chem. Soc. 125* (2003) 1134.

[4] R. Papadakis, *Chemical Physics 430* (2014) 29–39.

[5] P. Suppan, C. Tsiamis, *Spectrochim. Acta A, 36* (1980) 971.