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1. L. Antonov, G. Gergov, **V. Petrov**, M. Kubista and J. Nygren, *UV-Vis spectroscopic and chemometric study on the aggregation of ionic dyes in water*. *Talanta*, **1999**. 49(1): 99-106. **Цитати: 169^{*}; IF=4.16[†]**

Abstract: The monomer-dimer equilibrium in several ionic dyes (Methylene Blue, Acridine Orange, Nile Blue A, Neutral Red, Rhodamine 6G and Safranin O) has been investigated by means of UV-Vis spectroscopy. The data have been processed by a recently developed method for quantitative analysis of undefined mixtures, based on simultaneous resolution of the overlapping bands in the whole set of absorption spectra. In the cases of Acridine Orange a second chemometric approach has been used as a reference. It is based on a decomposition of the recorded spectra into a product of target and projection matrices using non iterative partial least squares (NIPALS). The matrices are then rotated to give the correct concentrations, spectral profiles of the components and the equilibrium constant. The dimeric constants determined by the two methods were in excellent agreement, evidencing the accuracy of the analysis. From the calculated dimeric constant and monomer and dimer spectra, the structures of the dimeric forms of the studied dyes are estimated.

2. **V. Petrov**, L. Antonov, H. Ehara and N. Harada, *Step by step filter based program for calculations of highly informative derivative curves*. *Computers and Chemistry*, **2000**. 24(5): 561-569. **Цитати:15; IF=1.92**

Abstract: We have developed a microcomputer program, based on a recently described approach called step by step filter (SBSF), for calculation of derivative curves directly from spectra recorded as a function of wavelength. This program avoids the long wavelength attenuation featured at conventional method for derivative curves calculation, and in this extent could be very helpful for daily spectroscopy practice. The features of the SBSF program include: easy treatment of data through a windowed environment, calculating of both conventional and step by step filter derivatives, possibilities for selection of the mathematical conditions for smoothing and differentiation simultaneous plotting of the original curve and its derivative and a mouse pointer. Several examples from different branches of the molecular spectroscopy (absorption UV-VIS, CD and fluorescence) are provided and discussed in the terms of advantages of SBSF.

3. L. Antonov and **V. Petrov**, *Quantitative analysis of undefined mixtures - "Fishing net" algorithm*. *Analytical and Bioanalytical Chemistry*, **2002**. 374(7-8): 1312-1317. **Цитати: 23; IF=3.43**

Abstract: An approach for quantitative analysis of mixtures with unknown individual responses of the components is discussed. although it is based on a resolution of overlapping bands technique, the main emphasis is not given to the computational facets of curve fitting. A logical procedure is described, allowing estimation of the unknown concentrations in the mixture, and both the number of overlapping bands and their assignment to the components in the solution to be determined automatically. A general conclusion about the precision of the method cannot be defined, because it depends on the extent of overlapping of the individual spectra of the components and their complexity. Using this procedure a complicated three-component acid-base equilibrium of a halochromic dye in solution is studied.

4. D. Antonova, L. Antonov, **V. Petrov**, V. Simeonov, S. Tsakovki, B. S. and W. Fluechiger, *Environmetric Assessment Of Pollutant Concentrations Effects On Forest Ecosystems*. *CHEMIA I Inzynierla Ekologiczna*, **2004**. 11(6). **Цитати: 2, IF=0.72**

Abstract: The present communication deals with the application of cluster and principal components analysis to a data set collected by monitoring wet precipitation at three different sampling sites. The idea is to identify latent factors responsible for the data structure at each site and, thus, to get information on their effects on the forest ecosystems. It

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has been found that a significant separation between the sites is achieved based on the analytical results and the identified factors correspond to acidic, mineral and crustal effects on the forest ecosystem.

5. F.S. Kamounah, L. Antonov, **V. Petrov** and G. Van Der Zwan, *An integrated approach to the study of the tautomerism of 4-((phenylimino)methyl) naphthalene-1-ol*. *Journal of Physical Organic Chemistry*, **2007**. 20(5): 313-320. **Цитати: 8; IF=1.34**

Abstract: The aim of the current report is to shed light on the tautomerism of 4-((Phenylimino)methyl) naphthalene-1-ol in solution, which was studied by UV-Vis spectroscopy and quantum chemical calculations. It was found that this compound does not have the typical tautomeric behavior of its analog 4-Phenylazo-naphthalen-1-ol. The complicated equilibrium between the enol- and keto-like forms and two kinds of dimers that can exist in solution, is strongly dependent on the proton acceptor/donor abilities of the solvent. Using advanced data treatment quantitative information about the tautomeric and dimeric equilibrium constants was obtained. Copyright © 2007 John Wiley & Sons, Ltd.

- 6*. **V. Petrov**, R. Gomes, A.J. Parola, A. Jesus, C.A.T. Laia and F. Pina, *2'-Hydroxyflavylium: introducing flavanones into the flavylium network of chemical reactions*. *Tetrahedron*, **2008**. 64(4): 714-720. **Цитати: 5; IF=2.66**

Abstract: Chalcones possessing a hydroxyl group in position 2 cyclize to form flavylium salts in acidic media, this reaction being reversible under neutral-basic conditions. On the other hand, chalcones possessing a hydroxyl group in position 2' cyclize to form flavanones in basic media. By synthesizing 2'-hydroxyflavylium tetrafluoroborate, it was possible to obtain trans-2,2'-dihydroxychalcone that in solution can evolve to 2'-hydroxyflavanone or back to 2'-hydroxyflavylium depending on the pH. The several equilibria established in aqueous solution were fully characterized. The importance of including flavanones into the flavylium network of chemical reactions is briefly exploited. © 2007 Elsevier Ltd. All rights reserved.

- 7*. **V. Petrov**, R. Gomes, A.J. Parola and F. Pina, *Flash photolysis and stopped flow studies of the 2'-methoxyflavylium network in aq. acidic and alkaline solution*. *Dyes and Pigments*, **2009**. 80(1): 149-155. **Цитати: 7; IF=3.47**

Abstract: The rate and equilibrium constants of the network of chemical species involving the dye 2'-methoxyflavylium tetrafluoroborate were characterized using stopped flow and flash photolysis in both acidic and alkaline aqueous solution. The trans-chalcone is the thermodynamic stable species in acidic solutions $2 < \text{pH} < 7$; irradiation of trans-chalcone at low pH leads to the corresponding coloured flavylium cation. The system reverts to its initial state in a few hours, in the dark. The kinetics of the various steps in the system were determined; flash photolysis revealed that the rate determining process of flavylium formation is the ring closure to give the corresponding hemiketal. In alkaline medium the ionized trans-chalcone is the stable form and clear evidence for the existence of a hemiketal species was obtained. A write-read-erase cycle can be performed with this compound. © 2008 Elsevier Ltd. All rights reserved.

- 8*. **V. Petrov**, C.A.T. Laia and F. Pina, *Photochromism of 7,4'-dihydroxyflavylium in an AOT reversed micelle system*. *Langmuir*, **2009**. 25(1): 594-601. **Цитати: 7; IF=3.93**

Abstract: The investigation of a flavylium compound in AOT reverse micelles shows photochromic enhancement in a wide pH range, with features previously unobserved in other colloidal systems. In equilibrium, 7,4'-dihydroxyflavylium transforms into tra/w-chalcone species at pH above 2, but ion-pair formation of the flavylium species with the negatively charged AOT is observed until pH = 5. After irradiation, trans-chalcone species are transformed with high quantum yields into both flavylium and its quinoidal base (through cis-chalcone and hemiketal species) until pH equal to 9. While trans-chalcone is located at the hydrophobic side of the reverse micelle interface, flavylium species tend to solubilize in the water pool. Flash photolysis experiments probe essentially the trans-chalcone solubilization site, showing that photochromic conversion to flavylium species can be achieved without acid catalysis with a unimolecular rate constant of 0.22 s^{-1} , while the slow recovery to equilibrium after irradiation probes essentially the water pool with a experimental pH-dependent rate constant. The photochromic mechanism is discussed, promising new insights about the possibility of changing the reversed micelle interfacial properties using photoresponsive additives like flavylium compounds. © 2009 American Chemical Society.

* Публикацията е включена в списъка за участие в конкурса.

9. L. Giestas, **V. Petrov**, P.V. Baptista and J.C. Lima, *General FRET-based coding for application in multiplexing methods*. Photochemical and Photobiological Sciences, **2009**. 8(8): 1130-1138. **Цитати: 4; IF=2.34**

Abstract: FRET can be used as a strategy to assign different simultaneous events in the same sample but "cross-talk" problems are a limitation. Here we present a contribution for the better understanding of the "cross-talk" in FRET experiments that include several pairs in the same sample. Using oligonucleotide probes labeled with fluorescent dyes which can be selectively excited at a specific wavelength, and using target oligonucleotides tagged with a fluorescent dye with specific characteristics that allow only it to emit light upon selective excitation of a specific probe by energy transfer (FRET), we aim to identify the exact probe-target hybridized pair. When using three donors to probe the presence of complementary targets, only 20% of possible donor/acceptor combinations give straightforward signals readily identifiable with the sample composition, while in the remaining cases severe cross-excitation prevents the direct identification of the sample composition. To correctly resolve the samples identity, we developed a theoretical model that enables the unequivocal attribution of a sample composition to a given set of fluorescence signals, in the presence of three donors. © 2009 The Royal Society of Chemistry and Owner Societies.

- 10*. **V. Petrov** and F. Pina, *Analytical resolution of the reaction rates of flavylum network by Laplace transform*. Journal of Mathematical Chemistry, **2010**. 47(3): 1005-1026. **Цитати: 7; IF=1.31**

Abstract: A complete resolution of time evolution for all species of flavylum chemical reactions network in acidic to neutral media was obtained applying Laplace transform methods, Vieta's formulae and the general partial fraction theorem. Analyses of particular systems under direct pH-jump, reverse pH-jump, stopped flow and flash photolysis experiments have been performed. The deduced formulas cover all possibilities of flavylum and anthocyanins compounds-with or without quinoidal base and with or without cis-trans isomerization barrier. The expressions for the observed rate constants in different type of experiments are quite similar. This allows creation of global procedure, based on fitting of one single set of expressions with data-set from different experiments. The mathematical approach allows easy and versatile programming. © 2009 Springer Science+Business Media, LLC.

- 11*. R. Gavara, **V. Petrov** and F. Pina, *Characterization of the 4'-hydroxynaphthoflavylum network of chemical reactions*. Photochemical and Photobiological Sciences, **2010**. 9(3): 298-303. **Цитати: 3; IF=2.34**

Abstract: The rate and equilibrium constants involved in the network of reactions of the 4'-hydroxynaphthoflavylum ion in moderately acidic and neutral media were characterized by means flash photolysis, stopped-flow and UV-vis absorption techniques. At the equilibrium, the network behaves as a two components system involving the naphthoflavylum ion and the trans-chalcone which is the thermodynamically stable species above pH = 2.9. All the rate and thermodynamic constants are very similar to those previously reported for 4'-hydroxyflavylum except the rate constant of the cis-trans isomerization which is much higher for the naphthoflavylum derivative. The lack of cis-trans isomerization barrier can be explained by the higher delocalization of the double bond between C(3) and C(4) charge through the naphthalene ring. Continuous irradiation experiments were carried out at the pH region that gives the higher photochromic efficiency. © 2010 The Royal Society of Chemistry and Owner Societies.

12. L. Cruz, **V. Petrov**, N. Teixeira, N. Mateus, F. Pina and V.D. Freitas, *Establishment of the chemical equilibria of different types of pyrananthocyanins in aqueous solutions: Evidence for the formation of aggregation in pyranomalvidin-3-O-coumaroylglucoside-(+)-catechin*. Journal of Physical Chemistry B, **2010**. 114(41): 13232-13240. **Цитати: 18; IF=3.18**

Abstract: The chemical equilibria of the pyranomalvidin-3-glucosides linked to (+)-catechin, (-)-epicatechin, and catechol moieties (and the respective coumaroylglucoside compounds) were established by means of UV-vis spectroscopy. The conjugated double bonds among pyranic rings C and D provide a higher electronic delocalization that prevents the nucleophilic attack of water at position 2. Consequently, besides flavylum cation (AH⁺), the bases A, A⁻, and A²⁻ have been identified by increasing pH, and the respective acidity constants were determined by spectrophotometry. The formation of dimers at higher concentration was observed for pyranomalvidin-3-O-coumaroylglucoside-(+)-catechin, and the respective data treated by the exciton model suggests the formation of a dimer where the monomers form J-type aggregates with the dipolar moments in opposite directions and rotated by 174° at a distance of 5.2 Å (from the center). © 2010 American Chemical Society.

13. F. Nave, **V. Petrov**, F. Pina, N. Teixeira, N. Mateus and V. De Freitas, *Thermodynamic and kinetic properties of a red wine pigment: Catechin-(4,8)-malvidin-3-O-glucoside*. *Journal of Physical Chemistry B*, **2010**. 114(42): 13487-13496. **Цитати: 15; IF=3.18**

Abstract: Catechin-(4,8)-malvidin-3-glucoside, a red pigment adduct (at acid pH) found in red wine and resulting from the reaction between malvidin-3-glucoside and flavan-3-ols during wine aging, was synthesized. The thermodynamic and kinetic constants of the network of chemical reactions were fully determined by stopped flow: (i) Direct pH jumps, from thermal equilibrated solutions at pH = 1.0 (flavylium cation, AH⁺), show three kinetic processes. The first one occurs within the mixing time of the stopped flow and leads to the formation of quinoidal bases A and/or A⁻ depending on the final pH; the second one takes place with a rate constant equal to $0.075 + 33[\text{H}^+]$ and was attributed to the hydration reaction that forms the pseudobases (hemiketals), B/B⁻. The third process is much slower, $2 \times 10^{-4} \text{ s}^{-1}$, and is due to the cis-trans isomerization giving rise to a small fraction of trans-chalcones, Ct/Ct⁻. (ii) Reverse pH jumps from the thermally equilibrated solution at moderate to neutral pH values back to a sufficiently acidic medium clearly distinguish three kinetic processes: the first one takes place within the dead time and is due to the protonation of the bases; the second process occurs with the same rate constant of the hydration reaction monitored by direct pH jumps and is attributed to the formation of flavylium cation from the B; the last process occurs with a rate constant of 1.8 s^{-1} , and results from the formation of AH⁺ from Ct through B, reflecting the rate of the ring closure (tautomerization). The separation of the hydration from the tautomerization upon a reverse pH jump is only possible because at pH < 1 the former reaction is faster than the last. An identical situation was observed for malvidin-3-glucoside (oenin) for pH < 2. © 2010 American Chemical Society.

14. J. Oliveira, **V. Petrov**, A.J. Parola, F. Pina, J. Azevedo, N. Teixeira, N.F. Brás, P.A. Fernandes, N. Mateus, M.J. Ramos, and V. De Freitas, *Chemical behavior of methylpyranomalvidin-3-O-glucoside in aqueous solution studied by NMR and UV-visible spectroscopy*. *Journal of Physical Chemistry B*, **2011**. 115(6): 1538-1545. **Цитати: 15; IF=3.18**

Abstract: In the present work, the proton-transfer reactions of the methylpyranomalvidin-3-O-glucoside pigment in water with different pH values was studied by NMR and UV-visible spectroscopies. The results showed four equilibrium forms: the methylpyranomalvidin-3-O-glucoside cation, the neutral quinoidal base, the respective anionic quinoidal base, and a dianionic base unprotonated at the methyl group. According to the NMR data, it seems that for methylpyranomalvidin-3-O-glucoside besides the acid-base equilibrium between the pyranoflavylium cation and the neutral quinoidal base, a new species is formed at pD 4.88-6.10. This is corroborated by the appearance of a new set of signals in the NMR spectrum that may be assigned to the formation of hemiketal/cis-chalcone species to a small extent. The two ionization constants (pKa1 and pKa2) obtained by both methods (NMR and UV-visible) for methylpyranomalvidin-3-O-glucoside are in agreement (pKa1 = 5.17 ± 0.03 ; pKa2 = 8.85 ± 0.08 ; and pKa1 = 4.57 ± 0.07 ; pKa2 = 8.23 ± 0.04 obtained by NMR and UV-visible spectroscopies, respectively). Moreover, the fully dianionic unprotonated form (at the methyl group) of the methylpyranomalvidin-3-O-glucoside is converted slowly into a new structure that displays a yellow color at basic pH. On the basis of the results obtained through LC-MS and NMR, the proposed structure was found to correspond to the flavonol syringetin-3-glucoside. © 2011 American Chemical Society.

- 15*. R. Gavara, **V. Petrov**, V. López and F. Pina, *Photochromism of naphthoflavylium. on the role of 4-OH hemiketal in flavylium network*. *Journal of Photochemistry and Photobiology A: Chemistry*, **2011**. 220(1): 4-10. **Цитати: 1; IF=2.63**

Abstract: Flavylium compounds suffer in aqueous solution the nucleophilic addition of water at moderately acidic pH values (hydration reaction). The hydration is possible in two positions, namely at position 2, forming hemiketal B2, and at position 4, forming hemiketal B4. B2 can subsequently evolve to give the cis- and trans-chalcone species. At the present work the network of chemical reactions involving the naphthoflavylium compound in aqueous solution was studied by means pH jumps, stopped flow, continuous irradiation and flash photolysis. The equilibrium and rate constants of the system were calculated through a mathematical model. The species B4 has a kinetic effect similar to the one observed for the quinoidal base (for flavylium dyes bearing acidic groups), i.e. B4 is a kinetic product retarding the rate of equilibration. Flash photolysis experiments in comparison with reverse pH jumps results show that the appearance of the flavylium ion is faster in the photochemical-induced process than in the thermal one, suggesting an additional photochemical pathway (besides photoisomerization) after the excitation of the trans-chalcone. © 2011 Elsevier B.V. All rights reserved.

- 16*. A.M. Diniz, C. Pinheiro, **V. Petrov**, A.J. Parola and F. Pina, *Synthesis and characterization of a symmetric bis(7-hydroxyflavylium) containing a methyl viologen bridge*. *Chemistry - A European Journal*, **2011**. 17(23): 6359-6368. **Цитати: 6; IF=5.32**

Abstract: A symmetric bis(flavylium) constituted by two 7-hydroxyflavylium moieties linked by a methylviologen bridge was synthesized. The thermodynamic and kinetics of the network of chemical reactions involving bis(flavylium) and the model compound 7-hydroxy-4'-methylflavylium was completely characterized by means of direct and reverse pH jumps (stopped flow) and flash photolysis. Both compounds follow the usual pH-dependent network of chemical reactions of flavylium derivatives. The equilibrium species of the model compound are the flavylium cation (acidic species) and the trans-chalcone (basic species) with an apparent $pK'_a=2.85$. In the case of the bis(flavylium) it was possible to characterize by ¹H NMR spectroscopy three species with different degrees of isomerization: all flavylium, flavylium-trans-chalcone, and all trans-chalcone. Representation of the time-dependent mole fraction distribution of these three forms after a pH jump from equilibrated solutions of all-flavylium cation (lower pH values) to higher pH values, shows that formation of trans-chalcone is not completely stochastic (two independent isomerizations), the isomerization of one flavylium showing a small influence on the isomerization of the other. The radical of the methyl viologen bridge is formed upon reduction of the bis(trans-chalcone) with dithionite. The system is reversible after addition of an oxidant in spite of the occurrence of some decomposition. Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

- 17*. S. Gago, **V. Petrov**, A.M. Diniz, A.J. Parola, L. Cunha-Silva and F. Pina, *Unidirectional switching between two flavylium reaction networks by the action of alternate stimuli of acid and base*. *Journal of Physical Chemistry A*, **2012**. 116(1): 372-380. **Цитати: 4; IF=2.85**

Abstract: The introduction of an ester group in the flavylium core allowed the reversible conversion between two different flavylium compounds each one exhibiting its own reaction network. An unidirectional switching cycle between 7-diethylamino-2-(4-(methoxycarbonyl)phenyl)-1-benzopyrylium and 2-(4-carboxyphenyl)-7-diethylamino-1-benzopyrylium was achieved by means of alternate acid and base stimuli. Addition of base to a methanolic solution of the ester derivative gives rise to the trans-chalcone of the parent carboxylic acid, which upon acidification of the solution forms the respective flavylium cation. This species esterifies under very acidic conditions to restore the original methyl ester derivative. The chemical reaction networks of both compounds were fully characterized from their thermodynamic and kinetic aspects, by a series of pH jumps followed by UV-vis absorption and emission spectroscopy, stopped flow and ¹H NMR. The crystal structure of the trans-chalcone of the ester derivative was unveiled showing a supramolecular structure involving hydrogen bonding. © 2011 American Chemical Society.

18. F. Pina, **V. Petrov** and C.A.T. Laia, *Photochromism of flavylium systems. An overview of a versatile multistate system*. *Dyes and Pigments*, **2012**. 92(2): 877-889. **Цитати: 22; IF=3.47**

Abstract: Flavylium is the basic structure of anthocyanins, an important family of natural dyes responsible for the color in many flowers and fruits. While anthocyanins in vitro are involved in a pH dependent equilibrium between a flavylium cation (acidic species) and a hemiketal (as major basic species), some synthetic flavylium compounds present the trans-chalcone as the major basic species. In this case irradiation of the trans-chalcone leads to appearance of colored products, either a flavylium cation and/or a quinoidal base, via cis-chalcone and hemiketal. Taking profit from the complexity of the network it is possible to design photochromic systems, exhibiting a thermal back reaction, or models for optical memories, when the back reaction is prevented. The flavylium photochromism was also observed in ionic liquids, gels, micelles and reversed micelles opening up possible applications. In this work an overview of the photochromism of synthetic flavylium compounds is presented, from the first observations of the light effect to recent developments. © 2011 Elsevier Ltd. All rights reserved.

- 19*. **V. Petrov** and F. Pina, *Complete resolution of the reaction Rates of flavylium Networks. The role played by 2-phenyl-2H-chromen-4-ol and the hydroxyl attack to the quinoidal Base*. *Journal of Mathematical Chemistry*, **2012**. 50(4): 1003-1019. **Цитати: 1; IF=1.34**

Abstract: Complete analytical resolution of the network of chemical reactions involving the flavylium compounds was achieved by means of the Laplace transform, general partial fraction theorem and Vieta's formulae. The kinetic model includes basic and acid catalysis of the hydration and tautomerization reactions. The formation of phenyl-2H-chromen-4-ol (B 4) and the role it plays in the kinetics in the case of compounds lacking of the hydroxyl substituents was also accounted for. In all cases four kinetic steps could be individualized and the pH dependent mole fraction distribution of the several species monitored as a function of time, the last one leading to the equilibrium. It is worth

of note the role of B 4 in the network, which like the quinoidal base is a kinetic product that retards the formation of Ct. The evolution of B 4 is also dependent on the existence or not of the cis-trans isomerisation barrier. Application of the model to the data of flavylum networks previously reported in literature, predicts with great accuracy the respective behavior. © 2011 Springer Science+Business Media, LLC.

- 20*. **V. Petrov**, A. Jorge Parola and F. Pina, *Isomerization between 2-(2,4-dihydroxystyryl)-1-benzopyrylium and 7-hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium*. *Journal of Physical Chemistry A*, **2012**. 116(31): 8107-8118. **Цитати: 5; IF=2.85**

Abstract: 2-Phenyl-1-benzopyrylium (flavylium) and 2-styryl-1-benzopyrylium (styrylflavylium) cations establish in aqueous solution a series of equilibria defining chemical reaction networks responsive to several stimuli (pH, light, redox potential). Control over the mole fraction distribution of species by applying the appropriate stimuli defines a horizontal approach to supramolecular chemistry, in agreement with the customary bottom-up approach toward complex systems. In this work, we designed an asymmetric styrylchalcone able to cyclize in two different ways, producing two isomeric styrylflavylium cations whose chemical reaction networks are thus interconnected. The chemical reaction networks of 2-(2,4-dihydroxystyryl)-1-benzopyrylium (AH⁺) and 7-hydroxy-2-(4-hydroxystyryl)-1-benzopyrylium (AH⁺ iso) comprise the usual species observed in flavylium-derived networks, in this case, the styryl derivatives of quinoidal bases, hemiketals, and chalcones. The thermodynamics and kinetics of the crossed networks were characterized by the use of UV-vis absorption and NMR spectroscopy as well as time-resolved pH jumps followed by stopped-flow. The two styrylflavylium cations are connected (isomerize) through two alternative intermediates, the asymmetric trans-styrylchalcone (Ct) and a spiropyran-type intermediate (SP). At pH = 1, AH⁺ slowly evolves (k_{obs} ≈ 10⁻⁵ s⁻¹) to a mixture containing 62% AH⁺ iso through the Ct intermediate, while at pH = 5, the SP intermediate is involved. The observed rate constants for the conversion of the styrylflavylium cations into equilibrium mixtures containing essentially Ct follow a pH-dependent bell-shaped curve in both networks. While at pH = 1 in the dark, AH⁺ evolves to an equilibrium mixture containing predominantly AH⁺ iso, irradiation at a > 435 nm induces the opposite conversion. © 2012 American Chemical Society.

- 21*. S. Gago, **V. Petrov**, A.J. Parola and F. Pina, *Synthesis, characterization and photochromism of 3'-butoxyflavylium derivatives*. *Journal of Photochemistry and Photobiology A: Chemistry*, **2012**. 244: 54-64. **Цитати: 3; IF=2.63**

Abstract: The compounds 3'-butoxy-7-methoxyflavylium and 3'-butoxy-7-hydroxyflavylium were synthesized and the respective equilibrium and rate constants determined by two complementary techniques, pH jumps and flash photolysis. An experimental strategy based on these two techniques allowed calculation of all the equilibrium and rate constants of the system carried out for the first time in flavylium compounds lacking of the high cis-trans isomerization barrier. Irradiation of the trans-chalcone gives rise to the formation of the cis-chalcone still during the lifetime of the flash, which disappears through two parallel reactions: (i) one leading to the recovery of the trans-chalcone and the other, (ii) forming flavylium cation via hemiketal. This last reaction is globally dependent on pH and at less acidic pH the system reverts back to the trans-chalcone. The highest yield of colour production upon the flash takes place in the pH range 2-3.5. © 2012 Elsevier B.V.

22. Y. Leydet, R. Gavara, **V. Petrov**, A.M. Diniz, A. Jorge Parola, J.C. Lima and F. Pina, *The effect of self-aggregation on the determination of the kinetic and thermodynamic constants of the network of chemical reactions in 3-glucoside anthocyanins*. *Phytochemistry*, **2012**. 83: 125-135. **Цитати: 36; IF=3.21**

Abstract: The six most common 3-glucoside anthocyanins, pelargonidin-3-glucoside, peonidin-3-glucoside, delphinidin-3-glucoside, malvidin-3-glucoside, cyanidin-3-glucoside and petunidin-3-glucoside were studied in great detail by NMR, UV-vis absorption and stopped flow. For each anthocyanin, the thermodynamic and kinetic constants of the network of chemical reactions were calculated at different anthocyanin concentration, from 6 × 10⁻⁶ M up to 8 × 10⁻⁴ M; an increasing of the flavylium cation acidity constant to give quinoidal base and a decreasing of the flavylium cation hydration constant to give hemiketal were observed by increasing the anthocyanin concentration. These effects are attributed to the self-aggregation of the flavylium cation and quinoidal base, which is stronger in the last case. The UV-vis and ¹H NMR spectral variations resulting from the increasing of the anthocyanin concentration were discussed in terms of two aggregation models; monomer-dimer and isodesmic, the last one considering the formation of higher order aggregates possessing the same aggregation constant of the dimer. The self-aggregation constant of flavylium cation at pH = 1.0, calculated by both models increases by increasing the number of methoxy (-OCH₃) or hydroxy (-OH) substituents following the order: myrtillin (2 -OH), oenin (2 -OCH₃), 3-OGI-petunidin (1 -OH, 1 -OCH₃), kuromanin (1 -OH), 3-OGI-peonidin (1 -OCH₃) and callistephin (none). Evidence for flavylium

aggregates possessing a shape between J and H was achieved, as well as for the formation of higher order aggregates.
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- 23°. R. Gavara, Y. Leydet, **V. Petrov** and F. Pina, *Photochemistry of 2-(4-hydroxystyryl)-1-naphthopyrylium*. *Photochemical and Photobiological Sciences*, **2012**. 11(11): 1691-1699. **Цитати: 6; IF=2.34**

Abstract: A new photochromic system based on 2-(4-hydroxystyryl)-1-naphthopyrylium encompasses the properties of the previously described naphthoflavylum and styrylflavylum systems. The photoproduct exhibits a colour deep in hue and is red shifted in comparison with the equivalent flavylum system. Reaction of 2-hydroxy-1-naphthaldehyde with p-hydroxystyrylmethylketone in acetic acid in the presence of tetrafluoroboric acid and acetic anhydride as catalysts leads to a mixture of two compounds: the photochromic 2-(4-hydroxystyryl)-1-naphthopyrylium and a second product 2-(4-acetoxystyryl)-1-naphthopyrylium resulting from the acetylation by acetic anhydride of the former. In acidic medium and at room temperature the hydrolysis of the acetoxy derivative leads to the 2-(4-hydroxystyryl)-1-naphthopyrylium, in circa 2 days, [HCl] = 0.25 M. The pH dependent chemical reactions taking place with 2-(4-hydroxystyryl)-1-naphthopyrylium were determined by UV-Vis, stopped flow, flash photolysis and ¹H NMR and follow the same general pattern of flavylum derivatives. In order to rationalize the photochromism, an energy level diagram summarizing all the equilibrium and rate constants of the network was drawn. © The Royal Society of Chemistry and Owner Societies 2012.

- 24°. A. Sousa, **V. Petrov**, P. Araújo, N. Mateus, F. Pina and V. De Freitas, *Thermodynamics, kinetics, and photochromism of oaklins: A recent family of deoxyanthocyanidins*. *Journal of Physical Chemistry B*, **2013**. 117(6): 1901-1910. **Цитати: 6; IF=3.18**

Abstract: Two oaklins guaiacylcatechinpyrylium (GCP) and syringylcatechinpyrylium (SCP) and a model compound deoxypeonidin (DOP) were synthesized, and the rate and equilibrium constants of the respective pH dependent network of chemical reactions were calculated. In contrast to anthocyanins, the three compounds possess a small cis-trans isomerization barrier and hence the rate of the trans-chalcone formation follows a bell-shaped curve as a function of pH. The three compounds exhibit photochromism obtained by irradiation of the trans-chalcone, which, depending on pH, leads to the colored species flavylum cation and quinoidal base. The flash photolysis together with pH jumps followed by UV-vis absorption and stopped flow is a very useful tool to achieve the rate and equilibrium constants of the network of chemical reactions followed by these molecules. Oaklin compounds which are formed in wine aged in oak barrels present physical-chemical properties more similar to simpler deoxyanthocyanidins rather than anthocyanins and may play a significant role in color changes observed in wine aging. Given their higher stability, they may be regarded as potential food colorants. © 2013 American Chemical Society.

- 25°. **V. Petrov**, R. Gavara, O. Dangles, S. Al Bittar, N. Mora-Soumille and F. Pina, *A flash photolysis and stopped-flow spectroscopy study of 3',4'-dihydroxy-7-O-β-d-glucopyranosyloxyflavylum chloride, an anthocyanin analogue exhibiting efficient photochromic properties*. *Photochemical and Photobiological Sciences*, **2013**. 12(3): 576-581. **Цитати: 5; IF=2.34**

Abstract: The complete determination of all rate and equilibrium constants of the network of reversible chemical reactions involving the anthocyanin analogue, 3',4'-dihydroxy-7-O-β-d-glucopyranosyloxyflavylum chloride, was achieved by means of UV-visible spectroscopy, flash photolysis and pH jumps monitored by stopped-flow. An energy level diagram containing all the data was obtained. A detailed step by step procedure illustrating all the calculations is reported. © 2013 The Royal Society of Chemistry and Owner Societies.

- 26°. R. Gavara, **V. Petrov**, A. Quintas and F. Pina, *Circular dichroism of anthocyanidin 3-glucoside self-aggregates*. *Phytochemistry*, **2013**. 88: 92-98. **Цитати: 7; IF=3.21**

Abstract: Self-association constants for the flavylum cations of the six most common anthocyanidin 3-glucosides were determined by circular dichroism (CD) and UV-Vis spectroscopy. Along with previous ¹H NMR results, all measurements were consistent with a monomer-dimer model. The CD spectra of the anthocyanidin 3-glucosides were similar to the analogues 3,5-diglucosides. All dimers of the anthocyanidin 3-glucosides exhibited left-handed CD signals, with petunidin-3-glucoside and myrtillin having the most intense signals. In addition, the magnitude of the molar ellipticity, [θ], was generally higher for the 3-glucosides than for the 3,5-diglucosides. For all six anthocyanins studied, the CD absorption spectra of their dimers showed evidence of the splitting of the monomer absorption into lower (J aggregates) and higher (H aggregates) energy bands. The angle and the distance between the dipolar

moments of the two monomers comprising the dimer were obtained from the lower energy absorption band. While the angle was more or less similar in all six dimers, the separation distance between the monomer dipole moments differed dramatically. The intensity of the CD signal displayed a linear dependence with the inverse square of the dipole moment distances. © 2013 Elsevier B.V. All rights reserved.

27. G. Calogero, A. Sinopoli, I. Citro, G. Di Marco, **V. Petrov**, A.M. Diniz, A.J. Parola and F. Pina, *Synthetic analogues of anthocyanins as sensitizers for dye-sensitized solar cells*. *Photochemical and Photobiological Sciences*, **2013**. 12(5): 883-894. **Цитати: 27; IF=2.34**

Abstract: Seven flavylum salt dyes were employed for the first time as sensitizers for dye-sensitized solar cells (DSSCs). The theoretical and experimental wavelengths of the maximum absorbances, the HOMO and LUMO energy levels, the coefficients, the oscillator strengths and the dipole moments are calculated for these synthetic dyes. The introduction of a donor group in the flavylum molecular structure was investigated. Photophysical and photoelectrochemical measurements showed that some of these synthetic analogues of anthocyanins are very promising for DSSC applications. The best performance was obtained by a DSSC based on the novel compound 7-(N,N-diethylamino)-3',4'-dihydroxyflavylium which produced a 2.15% solar energy-to-electricity conversion efficiency, under AM 1.5 irradiation (100 mW cm⁻²) with a short-circuit current density (J_{sc}) of 12.0 mA cm⁻², a fill factor of 0.5 and an open-circuit voltage (V_{oc}) of 0.355 V; its incident photocurrent efficiency of 51% at the peak of the visible absorption band of the dye is remarkable. Our results demonstrated that the substitution of a hydroxylic group with a diethylamine unit in position 7 of ring A of the flavylum backbone expanded the π -conjugation in the dye and thus resulted in a higher absorption in the visible region and is advantageous for effective electron injection from the dye into the conduction band of TiO₂. © 2013 The Royal Society of Chemistry and Owner Societies.

- 28*. A. Moro, A.M. Diniz, **V. Petrov** and F. Pina, *Chemistry of 7,8-dihydroxy-2-(4-dimethylaminostyryl)-1-benzopyrylium. A photochromic system switching from yellow to green*. *Journal of Photochemistry and Photobiology A: Chemistry*, **2013**. 263: 17-23. **Цитати: 0; IF=2.85**

Abstract: The bio-inspired compound 7,8-dihydroxy-2-(4-dimethylaminostyryl)-1-benzopyrylium (styrylflavylium) was synthesized through the insertion of a double bond between rings B and C of the flavylum cation. The pH dependent network of chemical reactions of the new compound is similar to the one of anthocyanins and related compounds. The styrylflavylium is the dominant species at very low pH values. At moderately acidic pH values the respective quinoidal base is formed by deprotonation of the styrylflavylium in competition with the hydration reaction to give an analogous of the anthocyanins hemiketal. The cis-chalcone is formed through the hemiketal (ring C opening) and the trans-chalcone by the cis-trans isomerization of the former. All the rate and equilibrium constants of these reactions have been calculated, permitting to completely characterize the styrylflavylium network. While in water no photochromism could be observed in the presence of CTAB micelles, formation of the flavylum cation upon irradiation of the trans-chalcone takes place. Complexation of the quinoidal base with Al³⁺ was clearly identified. © 2013 Elsevier B.V. All rights reserved.

- 29*. **V. Petrov**, A.M. Diniz, L. Cunha-Silva, A.J. Parola and F. Pina, *Kinetic and thermodynamic study of 2'-hydroxy-8-methoxyflavylium. Reaction network interconverting flavylum cation and flavanone*. *RSC Advances*, **2013**. 3(27): 10786-10794. **Цитати: 0; IF=3.11**

Abstract: 2'-Hydroxyflavylium and 2'-hydroxyflavanone derivatives can be interconverted by a precise sequence of pH jumps, through the respective intermediate (mono) ionized trans-chalcones. In acidic and neutral media, the well known network of chemical reactions involving flavylum cation, quinoidal base, hemiketal, and cis and trans chalcones is established. In the pH range 8 < pH < 10, the chalcone (Ct) deprotonates and evolves to the formation of a flavanone (F). At higher pH values, the di-ionized trans-chalcone is the stable species, formed from the flavylum cation. Acidification of the di-ionized trans-chalcone gives the flavylum cation or the flavanone, via the mono-ionized trans-chalcone, respectively at pH < 1 and pH \approx 9. In contrast with the chalcones, the flavanone once formed is stable even in acidic media. However, under strongly basic conditions, it leads back to the di-ionized trans-chalcone, the most stable species at more basic pH values, and the reactions leading to Ct-, F, Ct²⁻, Ct⁻, constitute a one direction cycle for interconversion of these species. © The Royal Society of Chemistry 2013.

30. F. Pina, **V. Petrov** and C.A.T. Laia, *Photochromism of flavylium systems. An overview of a versatile multistate system: Erratum: (Dyes and Pigments (2012) 92:2 (877-889))*. *Dyes and Pigments*, **2013**. 99(1): 256. **Цитати: 0; IF=3.47**

31. **V. Petrov**, S. Stanimirov, I.K. Petrov, A. Fernandes, V. De Freitas and F. Pina, *Emptying the β -cyclodextrin cavity by light: Photochemical removal of the trans -chalcone of 4',7'-dihydroxyflavylium*. *Journal of Physical Chemistry A*, **2013**. 117(41): 10692-10701. **Цитати: 13, IF=2.85**

Abstract: The interaction between the network of chemical reactions of the compound 4',7'-dihydroxyflavylium and β -cyclodextrin was studied by means of pH jumps, followed by UV-vis absorption, flash photolysis, stopped flow, and NMR. The trans-chalcone is the network species exhibiting the strongest interaction with the host. In moderately acidic medium, 95% of the trans-chalcone, 2.5×10^{-5} M, in the presence of β -cyclodextrin, 9×10^{-3} M, is expected to fill the host cavity (association constant 2.2×10^3 M⁻¹). In contrast, flavylium cation does not interact (association constant ≈ 0). Irradiation of the trans-chalcone in the presence of β -cyclodextrin 9 mM leads to the flavylium cation appearance. Light is thus capable of removing the trans-chalcone from the β -cyclodextrin, leaving the cavity empty. The system is reversible and trans-chalcone goes back to the initial state upon switching off the light due to the thermodynamic favorable conversion of flavylium cation to trans-chalcone in the presence of β -cyclodextrin. © 2013 American Chemical Society.

32*. L. Cabrita, **V. Petrov** and F. Pina, *On the thermal degradation of anthocyanidins: Cyanidin*. *RSC Advances*, **2014**. 4(36): 18939-18944. **Цитати: 6; IF=3.11**

Abstract: Cyanidin was studied by direct pH jumps (from equilibrated solutions at very low pH values to higher pH values) and reverse pH jumps (from equilibrated or not equilibrated solutions at higher pH values to very low ones). The kinetic steps of the direct and reverse pH jumps were followed by stopped flow, absorption spectroscopy and HPLC, at different timescales. The pH dependent rate constant of the slower kinetic process to reach the equilibrium follows a bell shaped curve as described for many synthetic flavylium compounds. Unlike anthocyanins, it was proved that there is no pH dependent reversibility in the system, since the chalcone suffers an irreversible degradation process. The mathematical expression to describe the bell shaped behaviour was deduced. These results contribute to explain why in plants glycosylation is crucial for the stabilization of the anthocyanins. © 2014 the Partner Organisations.

33*. **V. Petrov**, S. Slavcheva, S. Stanimirov and F. Pina, *Origin of the metastable stability in flavylium multistate systems*. *Journal of Physical Chemistry A*, **2015**. 119(12): 2908-2918. **Цитати: 2 IF=2.85;**

Abstract: Metastable states regarding the network of chemical reactions involving flavylium compounds were investigated as well as the role they may play in models for optical memories capable of write-read-erase. A necessary requirement to achieve metastable states in flavylium systems is the existence of a high cis-trans isomerization barrier, as in 4'-hydroxyflavylium described through this paper. In an optical memory, the metastable state could be the signal to be detected upon the write step. In that case the autoerase is prevented by the metastable state. Conversely, the metastable state may be the initial state and prevents the auto and unwanted write step. The compound 4'-hydroxyflavylium offers the possibility of achieving both of these two situations, depending on the sequence of the pH stimuli prior to light absorption. In this work the pH dependent distribution of the flavylium species of the network in the presence of β -cyclodextrin was calculated. Improvement of the performance of the photochromic system in the presence of β -cyclodextrin was observed. © 2015 American Chemical Society.

34. N. Basílio, **V. Petrov** and F. Pina, *Host-Guest Complexes of Flavylium Cations and Cucurbit[7]uril: The Influence of Flavylium Substituents on the Structure and Stability of the Complex*. *ChemPlusChem*, **2015**. 80(12): 1779-1785. **Цитати: 6; IF=3.24**

Abstract: The host-guest complexes formed from six differently substituted flavylium cations and cucurbit[7]uril (CB7) have been characterized by UV/Vis absorption, fluorescence emission and ¹H NMR spectroscopy. It was observed that all flavylium cations form 1:1 inclusion complexes with association constants that depend on the nature and position of the substituents. The results indicate that CB7 displays higher affinity for more hydrophobic flavylium

compounds and for those bearing amino substituents. ¹H NMR spectroscopy was used to elucidate the structure of the complexes. While for 7-hydroxyflavylium and 4-methyl-7-hydroxyflavylium the phenyl group (ring B) is included within the host's cavity leaving the benzopyrylium group (rings A and C) outside, in 4',7-dihydroxyflavylium and 3',4',7-trihydroxyflavylium the macrocycle shuttles between rings A and B. For compounds with amino substituents it was found that CB7 is attracted towards these groups regardless of their position in ring A or B. In addition, it was observed that the dimethylamino group tends to be positioned near the carbonyl-decorated portal while the diethylamino motif prefers the hydrophobic cavity of CB7. © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

35. N. Basílio, **V. Petrov** and F. Pina, *Corrigendum to: Host-Guest Complexes of Flavylium Cations and Cucurbit[7]uril: The Influence of Flavylium Substituents on the Structure and Stability of the Complex (ChemPlusChem, (2015), 80, (1779-1785), 10.1002/cplu.201500304)*. ChemPlusChem, **2016**. 81(11): 1136. **Цитати: 0; IF=3.24**

Abstract: Unfortunately, in Table 1 of the original article the association constants for the compounds 4'-MAHF and 4'-EAHF extrapolated for pH=1 are not correct. The correct values are $8 \times 10^6 \text{M}^{-1}$ and $5 \times 10^6 \text{M}^{-1}$ for 4'-MAHF and 4'-EAHF, respectively, and not $8 \times 10^5 \text{M}^{-1}$ and $5 \times 10^5 \text{M}^{-1}$ as originally reported. The corrected table is shown below. The discussion and conclusions were based on the correct values and therefore this error has no influence on them. We apologize to all readers for any inconvenience this error might have caused. (Table Presented). © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

36. J. Avó, **V. Petrov**, N. Basílio, A. Jorge Parola and F. Pina, *Evidence against the Twisted Intramolecular Charge Transfer (TICT) model in 7-aminoflavylium derivatives*. Dyes and Pigments, **2016**. 135: 86-93. **Цитати: 2; IF=3.47**

Abstract: A 4'-hydroxyflavylium bearing a julolidine (2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine) substituent in position 7 to minimize the amine rotation was characterized. Similarly to the 7-(N,N-diethylamino)-4'-hydroxyflavylium, the compound does not show trans-cis chalcone photoisomerization in water and the fluorescence emission quantum yield of its flavylium cation ($\Phi_f = 0.004$) is 2.5 times lower than the non-rigid analog. These results seem to exclude a Twisted Intramolecular Charge Transfer (TICT) model to explain the lack of photoisomerization of the chalcones and the small quantum yield of fluorescence emission in these compounds. The julolidine substituent is however slightly more efficient to prevent the hydration of the flavylium cation than the non-rigid amines. In both compounds hydration takes place only at basic pH values through the attack of the hydroxyl in position 2 of the quinoidal base. The chalcone forms of the julolidine derivative are unstable and decompose after several hours. The rate of flavylium formation from trans-chalcone is slow but increases directly with the mole fraction of protonated trans-chalcone for $1 < \text{pH} < 3$ and at higher proton concentrations it is proportional to $[\text{H}_3\text{O}^+]$ suggesting the existence of proton catalysis for the isomerization in the chalcone form. This catalytic effect of the proton is also observed in the compound 4',7-dihydroxyflavylium, showing that it is a more general phenomenon not related to the protonation of the amine substituent and not reported so far. © 2016 Elsevier Ltd

37. S. Gutzov, N. Danchova, R. Kirilova, **V. Petrov** and S. Yordanova, *Preparation and luminescence of silica aerogel composites containing an europium (III) phenanthroline nitrate complex*. Journal of Luminescence, **2017**. 183: 108-112. **Цитати: 0; IF=2.69**

Abstract: A simple two step procedure for the functionalization of hydrophobic silica aerogel microgranules with europium ions and/or 1,10 - phenanthroline is demonstrated. The activation procedure is based on soaking aerogels in a europium nitrate solution, followed by functionalization with 1,10 - phenanthroline. The functionalized materials display strong red or blue emission at UV-excitation, coming from the formation of $[\text{Eu}(\text{phen})_2](\text{NO}_3)_3$ or $\text{Si}(\text{IV})-1,10\text{-phenanthroline}$ complexes in the porous system of the aerogels. The most probable site symmetry of the europium cation is C_{2v} confirmed by luminescence spectra analysis. Room temperature diffuse reflectance spectra and excitation/luminescence spectra are used to describe the optical properties of the hybrid composites. Excitation spectra prove an efficient energy transfer between 1,10 - phenanthroline and the Eu^{3+} ion. © 2016