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#### **EDITORIAL**

### **President's Letter**

#### Dear EPA members

Time is flying and I am already reaching the end of my second year as EPA President. I have been in the Executive Committee (EC) of the EPA since the Grenada IUPAC meeting in 2004 and it is clearly time for me to step down. This will be officially done at the assembly of the General Council on July 16 in Coimbra during the XXIV IUPAC Symposium of Photochemistry. According to the statutes of our society, the president should be a member of the EC, as he should be well acquainted with the different activities and important issues concerning our society. The candidate to the next presidency is Werner Nau from the University of Bremen. He is now responsible for PPS matters after having been in charge of the public relations during several years. You will find his ideas about his role as EPA president in this issue of the Newsletter. Our past president, Dimitra Markovitsi, will leave the EC after having been successively editor of the Newsletter and President for three years. I wish to thank her warmly for all the energy she has devoted to make the EPA a lively society. Maybe a society can survive without a president but certainly not without a treasurer. Our treasurer, Silvio Canonica, will also step down from the EC. Silvio has been at this function since 1996 and thus I guess no further comment is needed to show his dedication to the EPA. I want to express my gratitude to him for all these years of continuous commitment. In order for the EC to work efficiently, two new members will join. As candidates, we propose Alexandre Fürstenberg, who has recently started his independent research in photobiology and biophysics at the University of Geneva, and Roberto Improta, from the CNR in Napoli, who is well known for his research in computational photochemistry. I am confident that they will bring additional energy for maintaining the activity of our society.

Alexandre Fürstenberg was one of the two laureates of the first EPA PhD prize. This year, we will award the third EPA prize to Karl Börjesson from Chalmers University in Göteborg for his work on fluorescent DNA probes. Whereas the EPA prize should be considered as an encouragement to a young and promising scientist,

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the Porter Medal is an acknowledgement to a photochemist for his achievements in the field. This year, the Porter Medal will be awarded to Thomas J. Meyer from University of North Carolina at Chapell Hill for his contributions to inorganic photochemistry and artificial photosynthesis. Finally, the EPA-PPS for the most cited research paper published in our journal by an EPA member in the 2009-11 period will be delivered to Mike Heilemann from the Julius-Maximilians-University in Würzburg for his article on subdiffraction fluorescence imaging (Photochem. Photobiol. Sci. 2009,**8**, 465-469). All three prize ceremonies will take place during the morning session of the IUPAC Symposium on Friday 20.

As you can see, there are many excellent reasons to go to Coimbra in July and I am looking forward to see you at this occasion.

Prof. Eric Vauthey Department of Physical Chemistry University of Geneva

### Letter of the President-Elect

I would like to thank the members of the Executive Committee (EC) of EPA for nominating me as future President of our society, with a two-year term of office foreseen from 2012-2014. Dimitra Markovitsi, our past President, and Eric Vauthey, our current President, have revived and consolidated EPA. During the past years, EPA has revised its statutes, introduced the award of Prizes, fostered contacts with companies, and added new force to the regular publication of the EPA Newsletter, developments which I have been able to actively contribute to as an EC member. A lively website has been reshaped (www.photochemistry.eu), and public relations have been advanced through the regular printing of flyers, the popularization of photochemistry in public and social events sponsored by EPA during international conferences. All of these goals could not have been achieved without an economic use of our limited budget, which, fortunately, is nowadays also sustained through an annual income from our journal, Photochemical and *Photobiological Sciences* (PPS), which the association can be proud to own. This additional financial contribution has allowed keeping membership fees constantly low for the past years.

Having been vice-chairman of the ownership board of PPS, I will remain member of the board during my upcoming term as president. The further development of the journal and the increased publication of work by EPA members in PPS will be one of my future tasks. It actually would take little but a sustained effort to change the status of PPS from "a" photochemistry journal to "the" photochemistry journal. Membership benefits, such as reduced conference fees at international photochemistry conferences and an increased recognition of the EPA Prizes are other areas that the EC will intensify its efforts on. New tools of efficient communication on photochemical topics must be tackled in the electronic information age, while traditional means such as the EPA Newsletter are presently being enriched by a competition for the best technical note. Unfortunately, the knowledge about EPA and its standing as a professional association varies quite markedly from one European country to another. This problem, which the EC is well aware of, goes hand in hand with the recognition of photochemistry as an attractive discipline in a particular country. Thus, making EPA better known will always have a positive impact on the recognition of our research field, as I am convinced, and this calls for some countryspecific activities, in addition to our efforts at the European level.

How can we win more scientists to become members of EPA? Being called a "photochemist" must become a distinction on its own. For this to be the case, photochemistry must not be associated with a specialized discipline or an outdated field, but rather an important hot topic, an investigative science on its own that offers viable approaches to the fundamental problem of improving sustainability. We don't exaggerate if we point out that the most important process on our planet is a photochemical one. We must claim back themes such as energy, even beyond photovoltaics and photosynthesis.

About 10 years back, I followed an invitation from the late Günther Otto Schenck, founder of the Max-Planck-Institute for radiation research, to his house in Mülheim, 2 years before he passed away. I stayed there for one night, and was listening closely to what he, the first one ever using a photochemical reaction for the commercial production of a chemical (ascaridol, 1948), had to tell a young photochemist. Schenck was a brilliant old man with many ideas, but I remember most vividly that he was utterly convinced that photochemists are predestined – with their interdisciplinary education in molecular as well as physical chemistry and with their deep appreciation for thermodynamics, whether in the form of redox potentials or photonic energy – to contribute to our world's energy problem. He suggested that photochemists should be nominated for advising politicians on energy matters. It is certainly something to think about!

In this spirit, I look forward to work with the newly elected EC for all EPA members and I would also like to express our gratitude to our General Treasurer Silvia Canonica and our past President Dimitra Markovitsi, the two EPA members whose term in the EC is foreseen to end this year.

> Prof. Werner Nau School of Engineering and Science of Chemistry Jacobs University, Bremen

### **GRAMMATICAKIS-NEUMANN PRIZE 2013**

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#### Call for Nominations

The Photochemistry Section of the Swiss Chemical Society (which acts as the Swiss section of the European Photochemistry Association, EPA) is pleased to invite nominations for the international Grammaticakis-Neumann Prize 2013.

The Prize consists of a diploma and a financial award of 5'000 Swiss Francs (for each awardee, if there is more than one), and it is presented once a year to a young research scientist (<40 at the time when he or she receives the prize) from academia or from industry, who does not hold a permanent or tenured position, for outstanding contributions to the science of photochemistry, molecular photobiology, or molecular photophysics.

The Prize, for which nominations are now being invited, will be presented during the 2013 Fall Meeting of the Swiss Chemical Society. The award ceremony will be followed by a lecture of the laureate.

Nominations are invited from organizations and individuals. Self-nominations are admitted.

- A nomination must include:
- 1) A brief curriculum vitae (max 2 pages).
- 2) A list of 5 of the nominee's most important scientific publications.
- 3) A nomination letter.
- 4) Not more than two seconding nomination letters

The documents listed under 1-3 should be sent electronically as a single pdf file to info@scg.ch (e.g. nominee name-Grammaticakis.pdf). Seconding letters should also be submitted electronically.

The closing date for nominations is September 30, 2012 (see also www.scg.ch/awards/grammaticakis.html).

Previous laureates of the Grammaticakis-Neumann Prize are Marina Kuimova (2011), Sivaguru Jayarman (2010), Alexander Heckel (2009), Alberto Credi (2008), Torsten Fiebig and Achim Wagenknecht (2007), Dario Bassani (2006), Johan Hofkens (2004), Nicola Armaroli

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(2002), Dirk Guldi (2001), Werner Nau and Eric Vauthey (1999), Axel Griesbeck (1997), Matthew Zimmt (1996). Luisa de Cola (1995), Pedro Aramendia (1994), Mark van der Auweraer (1992), V. Ramamurthy (1991), Wolfgang Rettig (1990), Martin Demuth (1987), Ian Gould and Anthony Harriman (1985).

In other years (e.g. 2000 and 2005) no prize was awarded, because no suitable candidate was proposed.

June 2012

### SPECIAL REPORT ON PHOTOCHROMISM

### Introduction

This issue of the EPA Newsletter has a special report on Photochromism. Starting from the last printed issue (June, 2011) we have introduced the thematic issues and suggestions for new themes are highly appreciated. The contributions on photochromism span various aspects of this active research area from basic principles and methods to actual applications. Jack Saltiel describes in his contribution the cis-trans photoisomerization of some diphenylpolyenes. Methodological aspects on how to analyse timeresolved data are covered by the contributions from Valentyn Prokhorenko and from Michel Sliwa, Stéphane Aloïse, and Cyril Ruckebusch. Finally, photochromism in action is described by the three contributions from Gianna Favaro, Ugo Mazzucato and Aldo Romani, from Arnaud Spangenberg, Jonathan Piard, Abhijit Patra, Rémi Métivier, and Keitaro Nakatani, and from Olga Fedorova.

We thank the authors for their nice contributions to this special issue.

Bo Albinsson Editor, EPA Newsletter

### The A and B of Cis-Trans Photoisomerization

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#### Jack Saltiel

#### Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390 USA

The focus of this contribution is on the photoisomerization mechanism of the first three members of the  $\alpha, \omega$ -diphenylpolyene series,  $C_6H_5(C=C)_nC_6H_5$ , n = 1-3, long studied as models for retinyl polyenes related to vitamin A and the visual pigments. Experimental evidence shows that the doubly excited singlet state,  $2^1A_g$ , is not involved in shaping the potential energy surface for the reaction and its formation does not facilitate photoisomerization. It is likely that torsional relaxation leading to photoisomerization occurs entirely in the  $1^1B_u$  excited singlet state.

In 1967 I proposed that cis-trans stilbene photoisomerization involves torsional relaxation to and decay from a global energy minimum (the phantom singlet,  ${}^{1}p^{*}$ ) in S<sub>1</sub>.<sup>1</sup> The complementarity of *trans*-stilbene,  ${}^{1}t^{*}$ , fluorescence and photoisomerization quantum



**Figure 1.** Birks' extension of the OS model for different relative energies of the 2 1Ag and 1 1Bu states; energy variation is shown along the torsional (isomerization) coordinate, cases (1) and (2) were proposed to apply to St and DPH, respectively.<sup>6</sup>

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yields and 1t\* lifetimes, over a wide T-range, were thus accounted for.<sup>2</sup> Fine tuning of the energetics of the potential energy curve, was accomplished when fluorescence studies revealed a small (0.2%) Tindependent adiabatic pathway to 1t\* from the cis isomer, 1c\*.3 Soon after Hudson and Kohler assigned the anomalous fluorescence of the vinylogous  $\alpha, \omega$ -diphenylpolyenes to emission from a forbidden doubly excited singlet state, 21Ag, lower in energy than the onephoton allowed 1<sup>1</sup>B<sub>u</sub> state,<sup>4</sup> Orlandi and Siebrand (OS) postulated a central role for that state in cis-trans photoisomerization.<sup>5</sup> OS attributed the intrinsic  ${}^{1}t^{*} \rightarrow {}^{1}p^{*}$  torsional barrier to crossing of the 11Bu and 21Ag potential energy surfaces and Birks extended this model to the higher members of the vinylogous series.<sup>6</sup> Case (1) in Fig. 1 depicts the OS model for the  ${}^{1}t^{*} \rightarrow {}^{1}p^{*}$  process in *trans*-stilbene (t-St) and case (2) shows the Birks extension of this model to photoisomerization of all-trans-1,6-diphenyl-1,3,5-hexatriene (ttt-DPH) and higher members of the series. Stronger vibronic coupling between the 11Bu and 21Ag states at the planar geometry was presumed to create the barrier along the torsional coordinate in case (2).6 In the following we reject the OS model and its extension by Birks, at least for the three lowest members of the diphenylpolyene series. We begin with *t*-St for which the  $1^{1}B_{u}$  state is S<sub>1</sub>, continue with ttt-DPH whose S<sub>1</sub> state is 2<sup>1</sup>A<sub>g</sub> and conclude with trans, trans-1,4diphenyl-1,3-butadiene (tt-DPB) for which the  $1^{1}B_{u}$  and  $2^{1}A_{g}$  states are close to isoenergetic.

t-St: The wide acceptance of the OS model is evident in the prominent role attributed to the 21Ag state in current literature.<sup>7</sup> Early objections to the OS model were based on theory: (1) For an  $A_{g}$ state to be involved in stilbene photoisomerization, it would have to be higher in energy than the 21Ag state.8 (2) The torsional barrier could be a property of the 11Bu state.9 Scrutiny of the OS model reveals that it is not consistent with experimentally determined torsional barriers in S<sub>1</sub> of *t*-St in solution and in the gas phase.<sup>10</sup> The 1<sup>1</sup>B<sub>u</sub> state is stabilized preferentially with increasing solvent polarizability.11 The expected stabilization of the 11Bu state relative to the 21Ag state on moving from the gas phase to a hydrocarbon solvent is ~5 kcal/mol. A 5 kcal/mol upward displacement of curve B in case (1) requires an earlier torsional transition state in the gas phase corresponding to a lower torsional energy barrier in  $S_1$  for *t*-St, but the barrier, if anything, increases from an intrinsic value of 2.8 kcal/mol (based on  $\Delta H$ , equivalent to a 3.3 kcal/mol Arrhenius

activation energy)<sup>2,3b</sup> in solution to 3.4 kcal/mol in the gas phase.<sup>12</sup> Congruence between theory and experiment was achieved recently in a high level theoretical paper that found no role for the  $2^1A_g$  state in St photoisomerization.<sup>13</sup>

*ttt*-DPH: The small torsional barrier expected from the interaction in case (2) is inconsistent with the longer fluorescence lifetimes of *ttt*-DPH (ns scale)<sup>14</sup> relative to *t*-St (ps scale)<sup>12</sup> in solution. Furthermore, Birks' assumption,<sup>6</sup> by analogy with the stilbenes, that all radiationless decay in the higher vinylogues involves torsional relaxation along photoisomerization coordinates is inconsistent with very small photoisomerization quantum yields.<sup>15</sup> In *ttt*-DPH,  $1^{1}B_{u}/2^{1}A_{g}$  equilibration is complete in the sub-ps time scale,<sup>16</sup> trans→cis photoisomerization activation energies far exceed the  $1^{1}B_{u}/2^{1}A_{g}$  energy gap<sup>15b</sup> and there is no significant change in photoisomerization efficiency when the  $1^{1}B_{u}/2^{1}A_{g}$  energy order is reversed in a rigid DPH analogue.<sup>17</sup> Easy access to the  $2^{1}A_{g}$  state does not facilitate photoisomerization and, if anything, impedes it.

**tt-DPB.** As for DPH, Birks assumed complementarity between fluorescence and photoisomerization pathways in applying the OS model to DPB.<sup>6,18</sup> With one notable exception,<sup>19</sup> subsequent investigators followed that practice,<sup>20-23</sup> despite early low photoisomerization quantum yields that suggest the presence of competing unreactive radiationless pathways.<sup>24,25</sup> *t*-St and *tt*-DPB photoisomerizations were used as probes for testing theories on medium effects on large amplitude motions. Discrepancies emerged in the interpretation of the influence of the medium on what



**Figure 2.** Medium effect on the lowest two singlet excited states of *tt*-DPB.<sup>25</sup>

appeared to be similar motions in the two molecules. tt-DPB  $\rightarrow$  ct-DPB quantum yields,  $\phi_{tt \rightarrow ct}$ , in hexane (H), cyclohexane (CH), benzene (Bz) and perfluorohexane (PFH) confirmed our suspicion that the discrepancies could be traced to assignment of all radiationless decay in *tt*-DPB to torsional relaxation. The  $\phi_{tt\to ct}$  values at 20 °C range from a high of 0.25 in Bz to a low of 0.076 in PFH.25 Figure 2 gives the relative energies of the  $1^{1}B_{u}$  and  $2^{1}A_{g}$  states in the four solvents. The changes reflect preferential stabilization of the 11Bu state with increasing medium polarizability. Photoisomerization is most efficient in the highly polarizable Bz in which the 1<sup>1</sup>B<sub>u</sub> state is the lowest excited singlet state and the  $\Delta E_{ab}$  gap is largest, and is least efficient in PFH where the 21Ag state is the lowest excited singlet state.<sup>25</sup> If the  $2^{1}A_{g}$  state were involved, photoisomerization would be most, not least, efficient in PFH whose radiationless decay is dominated by the  $1^1B_u \rightarrow 2^1A_g$  process. Here too, the Birks extension of the OS mechanism fails.

**Conclusion.** The  $2^{1}A_{g}$  state plays no role in the *trans*  $\rightarrow$  *cis* photoisomerization of the three lowest members of the  $\alpha,\omega$ diphenylpolyene series. Photoisomerization occurs in the 1'Bu state in all three. Beyond those generalities, the behaviour of each of the three is unique. Strict complementarity between fluorescence and photoisomerization via torsonal relaxation in S<sub>1</sub> applies only to *t*-St. radiationless decay channels not leading Significant to photoisomerization compete in the excited singlet state decay of tt-DPB and ttt-DPH. But, even tt-DPB and ttt-DPH exhibit strikingly different behaviour. In solution, and that also applies to PFH in which  $S_1$  is the  $2^1A_g$  state, all *tt*-DPB fluorescence is from the  $1^1B_u$ state. Vibronic coupling between the *tt*-DPB  $1^{1}B_{u}$  and  $2^{1}A_{g}$  states is not sufficiently strong to allow observation of the radiative decay of a mainly-A  $2^{1}A_{g}/1^{1}B_{u}$  mixed state. The opposite is true for *ttt*-DPH. Here 21Ag and 11Bu fluorescences are observed simultaneously from the equilibrated mixture of these two vibronically coupled states 10

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#### References.

1. (a) Saltiel, J. Perdeuteriostilbene. The Role of Phantom States in the Cis-Trans Photoisomerization of Stilbenes. J. Am. Chem. Soc. 89, 1036-1037 (1967). (b) Saltiel, J. Perdeuteriostilbene. The Triplet and

Singlet Paths for Stilbene Photoisomerization. J. Am. Chem. Soc. 90, 6394-6400 (1968).

2. Saltiel, J.; Charlton, J. L. Cis-Trans Isomerization of Olefins. In Rearrangements in Ground and Excited States; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol III, pp 25-89.

3. (a) Saltiel, J.; Waller, A. S.; Sears, Jr., D. F. The Temperature and Medium Dependencies of *vis*-Stilbene Fluorescence. The Energetics for Twisting in the Lowest Excited Singlet State. *J. Am. Chem. Soc.* **115,** 2453-2465 (1993). (b) Saltiel, J.; Waller, A. S.; Sears, Jr., D. F.; Garrett, C. Z. Fluorescence Quantum Yields of *trans*-Stilbene-d<sub>0</sub> and -d<sub>2</sub> in *n*-Hexane and *n*-Tetradecane. Medium and Deuterium Isotope Effects on Decay Processes. *J. Phys. Chem.* **97,** 2516-2522 (1993).

4. (a) Hudson, B. S.: Kohler, B. E. Linear polyene electronic structure and spectroscopy. *Annu. Rev. Phys. Chem.* **25**, 437-460 (1974). (b) Hudson, B. S.; Kohler, B. E.; Schulten, K. Linear polyene electronic structure and potential surfaces. In Excited States; E. C. Lim, Ed.; Academic Press: New York, 1982, Vol. 6, pp 1-95.

5. Orlandi, G.; Siebrand, W. Model for the direct photoisomerization of stilbene. *Chem. Phys. Lett.* **30**, 352-354 (1975).

6. Birks, J. B. Horizontal radiationless transitions. *Chem. Phys. Lett.* 54, 430-434 (1978).

7. See, e.g.: (a) Tzeli, D.; Theodorakopoulos, G.; Petsalakis, I. D.; Ajami, D.; Rebek, J., Jr. Conformations and Fluorescence of Encapsulated Stilbene, *J. Am. Chem. Soc.* **134**, 4346-4354 (2012). (b) Liu, F.; Morokuma, K, Computational Study on the Working Mechanism of a Stilbene Light-Driven Motor: Sloped Minimal Energy Path and Unidirectional Nonadiabatic Photoisomerization. *J. Am. Chem. Soc.* **134**, 4864-4876 (2012).

8. Hohlneicher, G.; Dick, B. Experimental Determination of the Low-Lying Excited A States of *trans*-Stilbene. *J. Photochem.* **27**, 215-231 (1984).

9. Troe, J.; Weitzel, K. M. MNDO Calculations of Stilbene Potential-Energy Properties Relevant for the Photoisomerization Dynamics. *J. Chem. Phys.* **88**, 7030-7039 (1988).

10. Turek, A. M.; Krishnamoorthy, G.; Sears, D. F., Jr.; Garcia, I.; Dmitrenko, O.; Saltiel, J. Resolution of Three Fluorescence Components in the Spectra of all-*trans*-1,6-Diphenyl-1,3,5-hexatriene under Isopolarizability Conditions. *J. Phys. Chem. A* **109**, 293-303 (2005).

11. Sklar, L. A.; Hudson, B. S.; Petersen, M.; Diamond, J. Conjugated polyene fatty acids as fluorescent probes: spectroscopic characterization. *Biochemistry* **16**, 813-818 (1977).

12. Saltiel, J.; Sun, Y.-P. Cis-Trans Isomerization of C,C Double Bonds. In Photochromism, Molecules and Systems, Dürr, H.; Bouas-Laurent, H. Eds.; Elsevier: Amsterdam, 1990, pp 64-164.

13. Minezawa, N.; Gordon, M. S. Photoisomerization of Stilbene: A Spin-Flip Density Functional Theory Approach. *J. Phys. Chem. A* **115**, 7901-7911 (2012).

14. Cehelnik, E. D.; Cundall, R. B.; Lockwood J. R.; Palmer, T. J. Solvent and temperature effects on the fluorescence of all-*trans*-1,6-diphenyl-1,3,5-hexatriene. *J. Phys. Chem.* **79**, 1369-1380 (1975).

15. (a) Saltiel, J.; Wang, S.; Watkins, L. P.; Ko, D.-H. Direct Photoisomerization of the 1,6-Diphenyl-1,3,5-hexatrienes. Medium Effect on Triplet and Singlet Contributions. *J. Phys. Chem. A* **104**, 11443-11450 (2000). (b) Saltiel, J.; Krishnamoorthy, G.; Huang, Z; Ko, D.-H.; Wang, S. The Photoisomerization of all-*trans*-1,6-Diphenyl-1,3,5-hexatriene. Temperature and Deuterium Isotope Effects. *J. Phys. Chem. A* **107**, 3178-3186 (2003).

16. Hogiu, S.; Werncke, W.; Pfeiffer, M.; Lau, A.; Steinke, T. Picosecond time-resolved CARS spectroscopy of a mixed excited singlet state of diphenylhexatriene. *Chem. Phys. Lett.* **287**, 8-16 (1998).

17. Saltiel, J.; Wang, S. The photochemistry and photophysics of all-trans-1,4-diindanylidenyl-2-butene, a rigid analogue of all-*trans*-1,6-diphenyl-1,3,5-hexatriene. *Photochem. Photobiol. Sci.* **5**, 883-895 (2006).

18. (a) Birks, J. B.; Birch, D. J. S. The Fluorescence of Diphenyl- and Retinol-Polyenes. *Chem. Phys. Lett*, **31**, 608-610 (1975). (b) Birks, J. B.; Tripathy, G. N. R.; Lumb, M. D. The Fluorescence of all-trans-Diphenylpolyenes. *Chem. Phys*, **33**, 185-194 (1978).

19. Velsko, S. P.; Fleming, G. R. Photochemical isomerization in solution. Photophysics of diphenylbutadiene. *J. Chem. Phys.* **76**, 3553-3562 (1982).

20. Birch, D. J. S.; Imhof, R. E. The Origin of Fluorescence from *trans,trans*-Diphenylbutadiene. *Chem. Phys. Lett.* **88**, 243-247 (1982).

21. (a) Gehrke, C.; Mohrschladt, R.; Schroeder, J.; Troe, J.; Vöhringer, P. Photoisomerization dynamics of diphenylbutadiene in compressed liquid alkanes and in solid environment. *Chem. Phys.* **152**, 45-56 (1991). (b) Mohrschladt, R.; Schroeder, J.; Schwarzer, D.; Troe, J.; Vőhriger, P. Barrier crossing and solvation dynamics in polar solvents: Photoisomerization of *trans*-stilbene and *E*,*E*- diphenylbutadiene in compressed alkanols. J. Chem. Phys. 101, 7566-7579 (1994). (c) Schroeder, J.; Steinel, T.; Troe, J. Quantitative Representation of Specific Rate Constants k(E) for the Photoisomerization of Diphenylpolyenes: The Solution of a Longstanding Problem. J. Phys. Chem. A 106, 5510-5516 (2002) and references cited.

22. (a) Anderton, R. M.; Kauffmann, J. E. Temperature-Dependent Rotational Relaxation of Diphenylbutadiene in n-Alcohols: A Test of Quasihydrodynamic Free Space Model. *J. Phys. Chem.* **98**, 12117-12124 (1994). (b) Anderton, R. M.; Kauffmann, J. E. Photoisomerization Rates of Diphenylbutadiene in n-Alcohols: Dielectric Dependent Activation Energies Determined via Fits to Kramers Expression. *J. Phys. Chem.* **98**, 12125-12132 (1994). (c) Anderton, R. M.; Kauffmann, J. E. Isodielectric Kramers-Hubbard Analysis of Diphenylbutadiene Photoisomerization in Alkyl Nitriles and Chlorinated Solvents. *J. Phys. Chem.* **99**, 14628-14631 (1995).

22. Dahl, K.; Biswas, R.; Maroncelli, M. The Photophysics and Dynamics of Diphenylbutadiene in Alkane and Perfluoroalkane Solvents. *J. Phys. Chem. B* **107**, 7838-7853 (2003)

23. Eastman, Jr., L. R.; Zarnegar, B. M.; Butler, J. M.; Whitten, D. G. An Unusual Case of Selectivity in a Photochemical Reaction. Photoisomerization of Unsymmetrical 1,3-Dienes. *J. Am. Chem. Soc.* **96**, 2281-2282 (1974).

24. Yee, W. A.; Hug, S. J.; Kliger, D. S. Direct and Sensitized Photoisomerization of 1,4-Diphenylbutadienes. J. Am. Chem. Soc. 110, 2164-2169 (1988).

25. Saltiel, J.; Krishna, T. S. R.; Laohhasurayotin, S.; Ren, Y.; Phipps, K.; Yee, W. A.; Davis, P. H. Medium Effects on the Direct Cis-Trans Photoisomerization of 1,4-Diphenyl-1,3-butadiene in Solution. *J. Phys. Chem. A* **115**, 2120-2129 (2011).

### Global Analysis of Multi-Dimensional Experimental Data

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Photochromism is essentially an equilibrium reaction of a medium upon absorption of a light energy resulting in transformation of several (at least two) chemical species, often due to reversible chemical reactions occurring under constant light illumination.<sup>1</sup> The relationship between initial (dark-adapted) and final (light-adapted) forms with different absorption spectra is dictated by the relationship of corresponding photochemical transfer rates between these forms. As such, this phenomenon is frequently investigated using a flashphotolysis or, more generally, pump-probe spectroscopy<sup>2</sup>, allowing identification of these transfer rates from measured time- and frequency-resolved spectra by applying a *global fit* approach where the spectra of an initial reactant, a terminal photoproduct (and the spectra of possible intermediates) can be recovered from the socalled Decay Associated Spectra (DAS) by means of target analysis.<sup>3</sup> In this approach the light-induced dynamics of an investigated medium is described as a sum of several spectral forms having distinguishable spectra with individual decay times:

$$F_{\lambda,t} = \sum_{i} A_{\lambda,i} D_{i,t} \ . \tag{1}$$

Here,  $F_{\lambda,t} \equiv F(\lambda_j, t_k)$  is a 2D-array of experimental data (e.g., differential absorbance in case of pump-probe spectroscopy) measured at given time delays {*t*} after excitation and detection wavelengths { $\lambda$ },  $A_{\lambda,i} \equiv A_i(\lambda_j)$  are the DAS, and  $D_{i,t}$  are the model response functions given via convolution integral of exponential decays with lifetimes  $\tau_i$  and instrument response function I(t):

$$D_{i,t} = I(t) \otimes e^{-t/\tau_i} \equiv \int_0^\infty dx I(t-x) e^{-x/\tau_i} .$$
 (2)

In the case of an infinity-short excitation pulse,  $D_{i,t} = \theta(t)e^{-t/\tau_i}$  where  $\theta(t)$  is the Heaviside step-function. The applicability of such an

approach originates from the Redfield theory<sup>4</sup> based on assumption of infinity-fast system-environment interaction.

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However, the observable changes to the induced absorbance can depend on the excitation wavelength as well<sup>4</sup>, so that in principle a full time- and frequency-resolved pump-probe (or fluorescence) experiment includes also the excitation wavelengths as well, i.e., measured array of experimental data has three dimensions (3D) instead of two:

$$F_{\lambda_d,\lambda_e,t} = \sum_i A_{\lambda_d,\lambda_e,i} D_{i,t} \quad , \tag{3}$$

where  $\lambda_d, \lambda_e$  are detection and excitation wavelengths, respectively. Unlike with 2D-experiment (Eq. 1) where individual DAS are vectors (one-dimensional arrays), description of a 3D-experiment is given by a set of two-dimensional DAS (2DDAS)  $A_{\lambda_d,\lambda_e,i}$ . However, since their kinetics still governed by the same model response decay function *D*, the global fit procedure, developed for 2D experimental data, can be generalized for case of multi-dimensional data arrays with the number of dimensions > 2 (e.g., 3D as in Eq. 3). This generalization, given below, will be illustrated for 3D-data arrays.

For the 2D-case, Eq. 1 can be written in a matrix form as  $F = A \times D$ . Multiplying by the inverse matrix  $D^{-1}$  from the right side gives the matrix of DAS vectors:  $A = F \times D^{-1}$  ( $D \times D^{-1} = 1$ ). Since the matrix of model response functions is strongly asymmetric (a few DAS and hundreds of delay times), it inversion can be obtained using a singular value decomposition.<sup>5</sup> In the indexing notation,

$$A_{\lambda,i} = \sum_{t} F_{\lambda,t} D_{t,i}^{-1} .$$
<sup>(4)</sup>

Fitting of model Eq. 1 to the data is performed by varying of lifetimes (free parameters) in the model response functions using minimization of a deviation between measured and calculated data (using Eq. 4) as a fit criterion<sup>6</sup>:  $\sum_{\lambda,t} (F_{\lambda,t} - \sum_{i} A_{\lambda,i}D_{i,t})^2 \rightarrow \min$ .

For the 3D-case, 2DDAS can be similarly obtained using, again, the inverse matrix of the model response functions:

$$A_{\lambda_d,\lambda_e,i} = \sum_{t} F_{\lambda_d,\lambda_e,t} D_{t,i}^{-1} .$$
(5)

The fit criterion is similar to 2D-case, but now the summation is performed over three dimensions<sup>7</sup>:

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$$\sum_{\lambda_d,\lambda_e,t} (F_{\lambda_d,\lambda_e,t} - \sum_i A_{\lambda_d,\lambda_e,i} D_{i,t})^2 \to \min \; .$$

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Generalization to N-dimensional experimental data  $F_{\lambda_1,\lambda_2,..\lambda_{N-1},t}$  is straightforward, and for ND-DAS we can write:

$$A_{\lambda_{1},\lambda_{2},..\lambda_{N-1},i} = \sum_{t} F_{\lambda_{1},\lambda_{2},..\lambda_{N-1},t} D_{t,i}^{-1} .$$
(6)

Note that the application of generalized global analysis of multidimensional experimental data is not limited by the flash-photolysis or time- and frequency-resolved fluorescence experiments. It is fully applicable for analysis of time-resolved diffraction experiments (Xray of electron diffraction) where the experimental data have more than two dimensions due to definition. The 3D global fit is also very useful for analysis of results of photon-echo based coherent multidimensional spectroscopy experiments.

#### References.

1. Glossary of Terms Used in Photochemistry (3<sup>rd</sup> edition). *Pure Appl. Chem.* **79**, 293–465 (2007).

2. P. Bonneau, J. Wirz, and A.D. Zuberbüller. Methods for the analysis of transient absorbance spectra. *Pure Appl. Chem.* **69**, 1-16 (1997).

3. I.H. van Stokkum, D.S. Larsen, and R. van Grondelle. Global and target analysis of time-resolved spectra. *BBA* **1657**, 82-104 (2004).

4. A.G. Redfield. On the theory of relaxation processes. *IBM Journal* 19-31 (1956). See also: K. Blum, Density matrix theory and applications. *Springer Verlag*, 1996, -323 p.

5. See the Matlab<sup>M</sup> documentation for built-in function SVD. See also in: M. Koerberg et al., Two dimensional transient absorption spectroscopy using a streak camera for detection and singular value decomposition for data analysis. *EPA Newsletter* **71**, 21-34 (2001).

6. This criterion is valid for the transient absorption (pump-probe) experiment. For fluorescence experiment one should be used instead

 $\sum_{\lambda,t} [(F_{\lambda,t} - \sum_i A_{\lambda,i} D_{i,t})/\sqrt{F_{\lambda,t}}]^2 \to \min \text{ due to Poisson statistics of noise.}$ 

7. A simple, Matlab<sup>™</sup>-based generic program for global fit of 3D time-resolved experimental data is available upon request to V.I.P., email address valentyn.prokhorenko@mpsd.cfel.de.

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### Multivariate curve resolution of time-resolved spectroscopy data to investigate photochromic molecules and derive photo-dynamical scheme.

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Time-resolved absorption technique is routinely used to study photochromic molecules and get detailed knowledge of their photodynamics.1 Indeed, time-resolved absorption of photo-switchable molecules enables to measure: 1) the photo-dynamics of the excited and intermediate species with femtosecond to millisecond time scale using optical laser pulses; 2) the formation and evolution of different photo-products with second to hour time scale using continuous irradiation. Thoroughly studies on different photochromic molecules (diarylethene, salicylidene aniline, chromene, spiropyrane...) have shown that photochromic scheme and photo-products are dependent of the excitation (wavelength and fluence) and of the environment (different solvents, encapsulation, embedded within a polymer...). As a result there exists usually many overlapping species (i.e. with neighbouring spectra or characteristic lifetimes) and only the combination of all the studies for various experimental conditions (wavelength range, time domain, etc.) allows to get an entire picture of the evolution of the studied photochromic molecules. Thus the main task remains to unravel the characteristic time profiles and spectra of the different photo-products.

Considering the analysis of time-resolved spectroscopy data, the most common method is the Global Lifetime Analysis (GLA), simultaneous analysis of multiple kinetic traces at different wavelengths.<sup>2</sup> This method provides a functional description of the kinetic profiles using exponential functions. The decay amplitudes are wavelength-dependent and constitute the so-called decay associated spectra. Nevertheless, some issues can be spotted regarding multiexponential fitting like the dependence of the results to initial estimates of the parameter, or the lack of flexibility of the method to integrate additional knowledge on the investigated processes (e.g., known spectra of some photoproducts obtained after chromatographic resolution) or to perform global analysis for various experimental conditions such as solvents, excitation wavelength, spectral domain, etc.. When a model is presumed from the findings of GLA, Global Target Analysis (GTA, one refers to Hard modelling approach)<sup>2</sup> can be performed providing kinetic parameters for the description of complex photochemical systems, to which species associated spectra are linked. However GTA encounters an intrinsic issue which is that a model should be built and validated for the ensemble of the investigated data. This is quite critical when the environment, solvent or the instrument has specific and complex response.

On the other hand soft modelling methods can be applied for the resolution of spectroscopy data probing complex evolving systems. Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS)<sup>3</sup> is one of the most widely used bilinear data decomposition method owing to its flexibility to integrate mathematical and chemical knowledge (so-called constraints) in both time and spectral direction. In time-resolved spectroscopy, timedependent concentration profiles C and spectra ST of the photochemical species are to be recovered from the sole measurement of the spectrokinetic data D (Figure 1). Additionally, a photo-dynamical scheme can be tested by implementing as an additional constraint a hard-model (HS-MCR). We already demonstrated the advantage of such technique to resolve ultrafast photochemistry of benzophenone and to identify a "hidden" intermediate in the relaxation process of the S1 state.<sup>4</sup> One important advantage for photochromic systems is the possibility to work with multiset structures, i.e. combining data coming from different experiments in order to provide a more complete and accurate description of the chemical system under study. As the different species and data matrices can be submitted to different constraints, enough flexibility is provided to combine complementary experiments (different excitations, different photo-products, etc.) or to apply a kinetic model to only some of the species/experiments in case a complete parametric description of the data is impossible or unlikely. We recently reviewed the advantage of MCR-ALS and HS-MCR to investigate ultrafast processes such as excited state intramolecular proton transfer (ESIPT) for photochromic salicylidene aniline SAOH.<sup>5</sup> As an example, only a multiset analysis allowed us to provide a full description of the 7 species after 266 nm

excitation and the existence of 2 parallel reactions (Figure 1). Two competitive processes were observed from the enol\* excited state: a rotation to get a cis-enol and an ESIPT followed by a cis-trans isomerization to get the trans-keto photochromic product. Resolution was finally achieved by MCR-ALS. The attribution of the intermediate species extracted was performed combining the results obtained for SAOMe (a substituted methylated molecule, for which one of the reaction pathways is prevented). The effect of inclusion on the photophysics of a substituted SAOH was also investigated with the help of MCR-ALS. The femtosecond transient absorption signal from the sample was extracted from the contribution of the strong excimer signal from toluene by multiset analysis which provided a way to characterize the formation of the final trans-keto form inside the capsule.6 The application of a multiset HS-MCR implementing a model only for SAOH after 390 nm excitation also shown great potential using solvent data (soft modelled) to handle femtosecond artifacts.



**Figure 1.** Multiset MCR-ALS analysis to unravel the photodynamical scheme for the photochromism of salicylidene aniline after 266 nm excitation.

The use of sensitive experiments (time scale and wavelength) should lead to a new way to analyze photochromic molecules, especially as nowadays new photochromic systems are developed for new applications (switching of fluorescence, magnetism, etc...) and their photo-dynamical are quite complex and strongly dependent of the condition (environment, excitation wavelength). The potential of

multivariate curve resolution methods to investigate ultrafast processes of photochromic molecules and derive a photo-dynamical scheme was recently demonstrated.<sup>4, 5, 6</sup> Furthermore this method should be even more useful for the analysis of time-resolved absorption data under continuous irradiation. Indeed it is easier to accumulate data with different experimental conditions making multiset analysis and implementation of chemical knowledge more powerful.

#### References.

1. Crano, J. C.; Guglielmetti, R. J., Organic Photochromic and Thermochromic Compounds; Plenum: New York, NY, (1999).

2. van Stokkum, I. H. M., Larsen, D. S., van Grondelle, R. *Biochimica Et Biophysica Acta-Bioenergetics* **1657**, 82-104 (2004).

3. de Juan, A., Tauler, R. Critical Reviews in Analytical Chemistry 36, 163-176 (2006).

4. Aloise, S., Ruckebusch, C., Blanchet, L., Rehault, J., Buntinx, G., Huvenne, J. P. *Journal of Physical Chemistry A* **112**, 224-231 (2008).

5. Ruckebusch, C., Sliwa, M., Pernot, P., de Juan, A. And Tauler, R. *Journal of Photochemsitry and Photobiology C: Photochemsitry Reviews* **13**, 1-27 (2012).

6. Sliwa, M., Naumov, P., Choi, H.-J., Quoc-Thiet, N., Debus, B., Delbaere, S., Ruckebusch, C. *ChemPhysChem* **12**, 1669-1672 (2011).

# Prototypes of bifunctional films with photochromic and electro-optical properties

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Production of materials which are able to modulate the light transmission by means of external electric fields and to change their color under light irradiation can be useful for a variety of applications, ranging from switching windows to large area panels for light transmission control. In the framework of our long-term project on the properties of photochromic compounds, we faced the problem of obtaining bifunctional films, which modulate their color by light and transparency by electric fields, in collaboration with a

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group of the University of Calabria having a great experience in the use of composite materials, such as polymer-dispersed or emulsiondispersed liquid crystals (PDLC or EDLC, respectively). A preliminary photochemical and kinetic study on some spiroindolinenaphtho-oxazine (SO)  $\rightarrow$  photomerocyanine (PM) photochromic systems (Scheme 1) in solution allowed a few photochromes to be selected offering the best compromise among the different good requirements for potential applications, namely photocolorability at room temperature and marked positive solvatochromism, with the color tunable from green to violet by changing from non-polar to polar media.1



**Scheme 1**. Typical SO  $\rightarrow$  PM photochromic reaction

This article describes two methods which were explored to prepare prototypes of bifunctional films, the normal and reverse modes.

Normal mode - A fluid EDLC (micron-sized liquid crystal droplets floating in an isotropic organic monomer) can be electrically switched from an opaque OFF state to a transparent ON state. In the absence of an electric field (OFF), the droplets are randomly aligned and the fluid films scatter light, due to the mismatch between the refractive indices of the liquid crystal and the monomer. Application of an electric field across the film (ON) aligns the director of the droplets parallel to the field. If a matching of the refractive indices is obtained, the film becomes transparent. In the presence of SO, UV-light stimulation triggers photocoloration, Fig. 1. Similar results were solid PDLC films prepared obtained by using by photopolymerization of the emulsion after adding an appropriate UV initiator.2

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**Figure 1.** Electro-optical response of an EDLC film containing SO (left) and coloration/decoloration cycles (right).

Reverse mode - A reverse mode operating PDLC film, which is transparent in its OFF state and electrically switchable into an opaque ON state, has attracted great attention for various potential applications. Our strategy to obtain a reverse mode device was to perform UV polymerization of the EDLC film containing SO in the presence of a magnetic field. When the latter, perpendicular to the cell substrates, is applied to the nematic emulsion, a homeotropic alignment (i.e. normal to the support) of the mesogenic molecules in the droplets, is induced and maintained even in the absence of the external field.<sup>3</sup> Fig. 2 shows the response of a PDLC film thus obtained. The plot on the right shows that the transmittance  $\tau_{decrease}$ , i.e. the time required by a sample to lose the homeotropic alignment, is practically unaffected by the SO percentage, whereas  $\tau_{rise}$  increases with % SO due to the progressively lower restoring force acting in the larger droplets.



**Figure 2.** Electro-optical response of a reverse mode PDLC film with 0.33% SO (left) and different SO percentages (right).

Bi-functional films display good electro-optical contrast, long term stability and uniform droplet size distribution, independent of the amount of SO dissolved. Compared with *normal-mode* films,<sup>2</sup> the photochemical process of the *reverse-mode* propotypes<sup>3</sup> was cleaner and the system exhibited better colorability and reversibility. These bifunctional devices are promising in the perspective of applications requiring a naturally transparent OFF state electrically switchable into an opaque ON state, as in the vehicles industry, building industry and agriculture (greenhouses).

#### References

1. Favaro, G., Chidichimo, G., Formoso, P., Manfredi, S., Mazzucato, U. & Romani, A. Chromatic and dynamic characteristics of some photochromes in the components of bifunctional photochromic and electro-optical devices. *J. Photochem. Photobiol. A: Chem.* **140**, 229-236 (2001) and references therein.

2. Chidichimo, G., Formoso, P., Manfredi, S., Favaro, G., Mazzucato, U. & Romani, A. Prototypes of bifunctional photochromic and electro-optical systems. *J. Appl. Phys.* **90**, 4906-4914 (2001).

3. Romani, A., Chidichimo, G., Formoso, P., Manfredi, S., Favaro, G. & Mazzucato, U. Photochromic behavior of a spiro-indolino-oxazine in reverse-mode polymer-dispersed liquid crystal films. *J. Phys. Chem. B* **106**, 9490-9495 (2002).

### Organic photochromic nanoparticles dispersed in water by laser ablation

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Laser ablation is a rather common method to produce metallic material. It was introduced about a decade ago in the world of organic materials, to fabricate suspensions of nanoparticles (NPs).<sup>1-2</sup> The procedure is rather simple: organic powder sample is introduced in a cuvette containing a solvent, which can be organic or aqueous. Under stirring, a pulsed laser beam is directed to the sample, and the

powder is fragmented into smaller particles (Fig. 1). After several minutes, the particles are small enough to be qualified as "nanoparticles". Optically, the initial turbid light-scattering medium becomes eventually translucent, and the suspension then looks like a solution, in which the molecules would have been "dissolved". When a nanosecond laser is used, the mechanism is photothermal: light is absorbed by the powder, and a sudden increase of temperature leads to its fragmentation. This happens above a given threshold fluence, and the wavelength of the laser has to be carefully chosen to match the absorption band of the compound. The solvent cools the NPs, which compensates the abovementioned heat, and the final size of the NPs is controlled by the balance between these two opposite factors.

There are various motivations to make such NP suspensions:

- Such suspensions look like clear solutions, just as if the organic molecules were dissolved in water. Whether it can be qualified as "green chemistry" or not, the use of organic solvents can be thus avoided.

- In NPs, light intensity attenuation is weak, and there are good probabilities that the whole material can be irradiated all through the particle, in particular for photochromic reactions.

- More generally speaking, photochromic systems do not behave the same way in solution and in the bulk state, and they may show other properties as NPs.

- By definition, the distance between the molecules in the NPs and the surface is in the nanometer range. This fundamental difference with other types of media brings some new expectations, related to a large area/volume ratio (e.g. in reactivity), or to nanometer-range interactions between the molecules inside and outside the NPs (e.g. in non-radiative energy transfer).

One can wonder whether the laser ablation method can be applied to photochromic systems or not, since an irradiation at the absorption wavelength of the A form is supposed to induce the A to B reaction. In fact, in most cases, over a given threshold (usually ca. 20 mJ.cm<sup>-2</sup> per pulse), both happen.<sup>3-6</sup> The initial turbid but colourless suspension becomes gradually clear, and the colour of the B form appears (Fig. 1). Also, under such high fluence, the photostationary state (PSS) is reached rather quickly (within a few minutes), but the fragmentation lasts for a longer time and the final size of the NPs is reached only after ca. 10 min. The NPs at the end EPA Newsletter

of the ablation procedure contains mainly the B form (sometimes up to 100%), and A form can be recovered by irradiation under visible light.

Several salicylidene-aniline and salicylidene-aminopyridine derivatives, also called anils, are T-type photochromes: the B form reverts back spontaneously (in the dark) to the A form. N-(3,5-di-*tert*-butylsalicylidene)-4-aminopyridine (DBSAP) shows photochromism both in organic solution (acetonitrile, cyclohexane, ethanol, etc.) and in the bulk state. The kinetic of the thermal back reaction is so fast in solution, that the red color of the B form cannot be seen by the naked eye. At the opposite, in the bulk state, it takes several months for B to fade. Despite the weakness of anils against hydrolysis, we succeeded in obtaining NPs in a water-surfactant (Triton X reduced) medium under irradiation with a 355 nm nanosecond laser (Fig. 1).<sup>3</sup>



Fig. 1: Laser ablation of DBSAP: experimental conditions, and images before and after the laser ablation process.

Regarding the kinetics of the thermal back reaction, we got an intermediate result in the NP form, showing the possibility to tune this parameter for a given molecule. For applications in variable transmission materials, the control of this parameter is an important issue.

State	Thermal reaction kinetic constants /s <sup>-1</sup>	Fading of B form
EtOH solution	320	n.a.
Nanoparticles	2.6.10-3 (25%)	A few hours
	3.2.10-4 (75%)	
Bulk solid	3.6.10-5 (1%)	Several months
	1.8.10 <sup>-8</sup> (99%)	

1,2-bis(5'-ethoxy-2'-(2"-pyridyl)thiazolyl)perfluorocyclopentene is a diarylethene (DAE), which shows photochromism both in organic solvents and in the bulk state.<sup>4</sup> In solution, an equilibrium between the parallel and anti-parallel conformers is usually seen. Both absorb at the same wavelength, but only the latter undergoes the expected ring-closure reaction. As a consequence, a large proportion of the photons are wasted, and the quantum yield cannot exceed 50% if both conformers are present in equal amounts (Fig. 2). In chloroform solution, the quantum yield of the A to B reaction is 32%. NPs were fabricated (nanosecond laser, 355 nm), and single particle experiments allowed us to evidence the photochromic character of the NPs. The A to B reaction quantum yield in this form was raised up to 60% in NPs. X-ray diffraction shows that the bulk material is made of 100% anti-parallel conformation (to be compared to 50% in solution). The high quantum yield in NPs might stem from this structural feature, assuming that the bulk structure is preserved in NPs.



Fig. 2: Photochromism in DAE molecules, the anti-parallel conformation is reactive whereas the parallel one is not.

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Another noteworthy result is that laser ablation can be carried out at a wavelength where the B form absorbs, but A does not. In fact, when an irradiation by a 532 nm nanosecond laser is combined with a 365 nm beam (Hg/Xe lamp) to evolve in situ the B form, an efficient fragmentation occurs.

The combination of photochromic and fluorescent properties for fluorescence switching is a very active field of research.7 The A form of 1,2-bis[4'-methyl-2'-(2"-pyridyl)thiazolyl]perfluorocyclopentene is fluorescent, and an UV irradiation induces a large drop, concomitantly to the A to B reaction.5 The fluorescence quantum yield, however, drops by a factor of 40 between the bulk solid and the solution. On the other hand, this molecule is photochromic in organic solution (e.g. acetonitrile), but apparently not seen in the bulk state, preventing from any possibility to perform efficient fluorescence photoswitching. By making NPs, we found a trade-off situation: although less efficient than in solution, photochromism with a significant conversion (63% conversion at PSS under 365 nm irradiation) was obtained in NP suspensions. Moreover, the fluorescence could be switched, with an intensity contrast of ca. 50%. The NPs were characterized by combined fluorescence microscopy and atomic force microscopy (AFM). These nanomaterials represent a first attempt to highlight attractive properties of molecular photochromic NPs to be employed as efficient photoswitchable single emitters.



Fig. 3: Fluorescence and AFM images of 1,2-bis[4'-methyl-2'-(2"pyridyl)thiazolyl]perfluorocyclopentene NPs.

As a conclusion, the laser ablation method was successfully applied on several photochromic molecular systems. One has to mention that several other techniques, such as the well-known reprecipitation method, usually lead to narrower size distributions. However, laser ablation is very much easy to control, the production of photochromic NPs is efficient and reproducible, tunable sizes and morphologies may simply be obtained by changing the laser fluence or exposure time, size evolution is negligible (most often), and last but not least, very high concentration of NPs is allowed by this method. All these arguments make the laser ablation a method of choice in the field of photoactive nanomaterials. Nevertheless, laser ablation still needs to be understood in depth, finely tuned and improved, especially for the synthesis of very small and monodisperse NPs, and further exploited in order to be applied to a wide range of organic photochromic compounds. The examples presented in this article bring some evidence of the attractiveness of NPs in the world of photochromism. They provide specitic features, and may contribute to tune the properties, according to the targeted application.

#### References.

1. Tamaki, Y., Asahi, T. & Masuhara H. Appl. Surf. Sci., 168, 85-88 (2000).

2. Asahi, T., Sugiyama, T. & Masuhara, H. Acc. Chem. Res., 41, 1790-1798 (2009).

3. Patra, A., Métivier, R., Piard., J. & Nakatani, K. *Chem. Commun.*, 46, 6385-6387 (2010).

4. Spangenberg, A., Métivier, R., Gonzalez, J., Nakatani, K., Yu, P., Giraud, M., Léaustic, A., Guillot, R., Uwada, T. & Asahi, T. *Adv. Mater.*, **21**, 309-313 (2009).

5. Piard, J., Métivier, R., Giraud, M., Léaustic, A., Yu, P. & Nakatani, K. *New J. Chem.*, **33**, 1420-1426 (2009).

6. Patra, A., Métivier, R., Brisset, F. & Nakatani, K. *Chem. Commun.*, **48**, 2489-2491 (2012).

Fukaminato, T., J. Photochem. Photobiol. C, 12, 177-208 (2001). Irie,
 M., Photochem. Photobiol. Sci., 9, 1535-1542 (2010). Tian, Z., Wu, W. &
 Li, A.D.Q., ChemPhysChem, 10, 2577-2591 (2009). Tian H. & Wang,
 S., Chem. Commun., 781-792 (2007). Raymo, F.M. & Tomasulo, M.
 Chem. Soc. Rev., 34, 327-336 (2005).

#### Photocontrolled DNA-binding ligands

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Spatial and temporal control of properties in biological systems by photochromic compounds attained a great interest in recent years [1]. DNA-binding ligands are among the most promising candidates as chemotherapeutic anticancer, antiviral or antibacterial drugs, because the physiological function of DNA may be changed or suppressed drastically by groove-binding or intercalating ligands. A main challenge with respect to the application of such drugs is the spatial and temporal control of the drug-DNA interaction, because the regulation of the drug activity will enable a highly selective chemotherapeutic approach. Owing to their ability to transform upon irradiation into planar forms, some photochromic compounds may be used for reversible photo-control of intercalation into DNA. Recently, it has been demonstrated that the DNA- and RNA-binding properties of photochromic spiropyran derivatives are controlled by irradiation, namely a non-intercalating spiropyran is transformed to the intercalating merocyanine upon irradiation with UV light [2,3]. The photochromic properties of a chromene derivative, that contains a positively charged substituent, were investigated in the presence of ctDNA (fig. 1) [4]. Upon irradiation in the absence of DNA the colored quinoid open form is highly unstable and rapidly reverts back to the initial closed form (bleaching). In the presence of DNA the



**Figure 1.** A schematic showing the DNA – chromene interaction and the change of fading rate constant value upon the intercalation.

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Figure 2. A schematic showing the DNA-ligand interaction *in situ* with temporal control.

open form is significantly stabilized, presumably because of the association with the macromolecule. The kinetics of the bleaching reaction of the bound ligand were determined and employed to estimate the binding constant.

The photoinduced transformation of the styrylbenzothiazole derivative into the corresponding DNA-binding benzothiazoloquinolinium represents a new examples for a system that may be used for the *in situ* generation of a DNA intercalator [5]. Notably, the ligand may be formed directly in the presence of DNA so that temporal and spatial control of the DNA-ligand interaction is possible (fig. 2).

#### References.

1. G. Mayer, A. Heckel, Angew. Chem. Int. Ed., 2006, 45, 4900-4921.

2. M. Hammarson, J. Andersson, S. Li, P. Lincoln, J. Andréasson, *Chem. Commun.*, 2010, 46, 7130-7132.

3. D. D. Young, A. Deiters, ChemBioChem, 2008, 9, 1225-1228.

4. S. V. Paramonov, V. Lokshin, H. Ihmels, O. A. Fedorova, J. Photochem. Photobiol. Sci. 2011, 10(8),1279-82.

5. Daria Berdnikova, Olga Fedorova, Elena Gulakova, Heiko Ihmels, *Chem. Commun.*, 2012, *48(38)*, 4603-4605.

### PUBLICATIONS

### Abstracts of Theses in Photochemistry

### Oksana Kel

Ultrafast excited-state dynamics of new chromophoric systems developed for specific applications

#### Department of Physical Chemistry, University of Geneva PhD thesis: 2012 Research Advisor: Prof. Eric Vauthey

The subject of this thesis is the investigation, using a variety of ultrafast spectroscopic techniques, of the excited-state properties of two families of new compounds, one developed for potential applications in photovoltaics and the other synthesised for the elaboration of new fluorescent chiral probes.

The development of smart artificial photosystems, which convert solar energy into chemical energy with high efficiency is an issue of increasing importance. Multichromophoric compounds consisting of amino naphthalene diimides (NDI) covalently attached to a poctiphenyl (POP) scaffold have been shown to self-assemble as supramolecular tetramers in lipid bilayer membranes and to generate a transmembrane proton gradient upon photoexcitation.<sup>1</sup> By slight chemical modifications on the NDI core subtitutuents, the photophysical properties of the molecule change dramatically and access to all the visible sunlight at high extinction coefficients is provided.<sup>2</sup> Moreover, NDIs covalently attached to POP and oligophenylethynyl (OPE) scaffolds can be self-organized as zipper assembly on a gold surface, thereby providing materials with a spatially ordered and oriented redox gradient.<sup>3</sup>

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**Figure 1.** Structure of the multichromophoric systems (R/R'=OEt/OEt, NHiPr/Br, NHiPr/OEt; X=NH<sub>3</sub><sup>+</sup>, (benzyloxy)carbonyl)

Using femtosecond transient absorption (TA) and fluorescence upconversion techniques, we evidenced the population of a chargeseparated state upon excitation of multichromophoric NDIs systems with different substituents covalently attached to a POP or OPE scaffold (Figure 1). Depending on the type of scaffold, NDI core substituents, and excitation wavelength, two charge separation (CS) pathways have been demonstrated: 1) symmetry-breaking CS between two NDI units and 2) CS between a NDI and the scaffold.<sup>2,4</sup> The obtained results highlight the power of NDI multichromophoric systems for photovoltaic application, namely for constructing supramolecular n/p-heterojunctions. The main features of these NDIs multichromophoric systems is that they act at the same time as antenna (harvesting optical energy) and as reaction center (undergoing charge separation), contrary to other multichromophoric systems presented in the literature. EPA Newsletter

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Figure 2. Structure of a two-colour SOSIP architecture

The first prototypes of supramolecular n/p-heterojunction solar cells constructed from NDIs showed promising results. Systems realized by self-organizing surface-initiated polymerization (SOSIP) of NDI on a transparent electrode (ITO) (Figure 2) have been investigated. The TA measurements of single-colour SOSIP architectures indicate that the origin of photocurrent generation upon excitation is a symmetry-breaking CS between two NDIs.<sup>5</sup> In two-colour SOSIP architectures, additional CS pathways between different NDIs were also evidenced. Many parameters such as the type of NDIs, the distance between them, NDI sequence, etc. have an important impact on the CS efficiency in these architectures.

Chirality plays an important role in the recognition processes between biological molecules such as, e.g., protein – DNA interaction, enzymatic catalysis, antibody activity. Therefore, the molecular mechanisms involved in these specific interactions have been attracting strong interest. Cationic [4]helicene derivatives (HelR) have a polycyclic aromatic and positively charged structure (Figure 3), which make them attractive chiral DNA binding agents. Helicenes have been shown to be highly specific chiral probes, able to recognize the polymorphism of DNA structures including Z-DNA. Their charged analogs presented in this thesis have been synthesized and their photophysics studied for the first time.



HelMe: R=CH3, A=BF4, Cl

HelPr: R=(CH2)2CH3, A= Cl-

HelOH: R=(CH2)2OH, A- CH3COO-

Figure 3. [4] helicene cations (HelR)

Using steady-state and ultrafast fluorescence methods, features of [4]helicene dimers have been observed in water solution. This aggregation changes the photophysical properties of the investigated compounds, i.e. spectral shape of absorption and fluorescence, fluorescence lifetime, quantum yield and anisotropy decay.<sup>6</sup>

In the presence of salmon sperm DNA, the absorption and fluorescence spectra of the [4]helicene derivatives change significantly. The fluorescence quantum yield increases with addition of DNA and a new long-lived decay component appears in the fluorescence dynamics. This longer lifetime corresponds to HelR bound to DNA. The binding constants were measured for racemic and both enantiopure forms using a fluorescence titration method. This experiment shows that the [4]helicene derivatives are binding stereoselectively to DNA: the (M)-enantiomer interacts more efficiently with salmon sperm DNA than the (P)-enantiomer, independently of the substituents on the nitrogens. Linear dichroism (LD) experiments revealed that HelR binds on the groove of double strand DNA. The obtained results suggest [4]helicene derivatives as potential near infrared fluorescence probes with a broad applicability in chemistry, biology and medicine. Variation of the substituents opens the door to other dyes with specific sensing properties.

(1) Bhosale, S.; L., S. A.; Talukdar, P.; Fürstenberg, A.; Banerji, N.; Vauthey, E.; Bollot, G.; Mareda, J.; Röger, C.; Würthner, F.; Sakai, N.; Matile, S. Photoproduction of proton gradients with pi-stacked fluorophore scaffolds in lipid bilayers. *Science* **2006**, *313*, 84-86.

(2) Bhosale, R.; Kishore, R. S. K.; Ravikumar, V.; Kel, O.; Vauthey, E.; Sakai, N.; Matile, S. Zipper assembly of SHJ photosystems: focus on red naphthalenediimides, optoelectronic finetuning and topological matching. *Chem. Sci.* **2010**, *1*, 357-368.

(3) Bhosale, R.; Perez-Velasco, A.; Ravikumar, V.; Kishore, R. S. K.; Kel, O.; Gomez-Casado, A.; Jonkheijm, P.; Huskens, J.; Maroni, P.; Borkovec, M.; Sawada, T.; Vauthey, E.; Sakai, N.; Matile, S. Topologically Matching Supramolecular n/p-Heterojunction Architectures. *Angew. Chem. Int. Ed.* **2009**, 6461-6464.

(4) Kishore, R. S. K.; Kel, O.; Banerji, N.; Emery, D.; Bollot, G.; Mareda, J.; Gomez-Casado, A.; Jonkheijm, P.; Huskens, J.; Maroni, P.; Borkovec, M.; Vauthey, E.; Sakai, N.; Matile, S. Ordered and oriented SHJ surface architectures: completion of the primary color collection. J. Am. Chem. Soc. 2009, 131, 11106-11116.

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(5) Sakai, N.; Lista, M.; Kel, O.; Sakurai, S.-i.; Emery, D.; Mareda, J.; Vauthey, E.; Matile, S. Self-Organizing Surface-Initiated Polymerization: Facile Access to Complex Functional Systems. *J. Am. Chem. Soc.* **2011**, *133*, 15224-15227.

(6) Kel, O.; Sherin, P.; Mehanna, N.; Laleu, B.; Lacour, J.; Vauthey, E. Excited-state properties of chiral [4]helicene cations. *Photochem. Photobiol. Sci.* **2012**, *11*, 623-631.

#### Technical notes

### Purification processes for nanoparticles: centrifugation vs. filtration

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Nanotechnology has revolutionized many areas of science and of daily life<sup>1-3</sup>. The dramatically increase of the applications in which nanoparticles are employed is directly link to the ability to carefully tune their features (optical, catalytic, etc.) by the synthetic processes used to produce nanostructures with well-definite geometry and size<sup>4-5</sup>. One of the key goals in the realization of effective nanoparticles or to completely characterize them is the use of the best purification process, which is able to purify particles from the "unwanted" molecules with less possible product-loss. Generally, the more useful methods in this sense are either centrifugation or filtration processes (two methods ordinary used in molecular biology).

In this technical note I would like to share the experiences I gained in the last years on this field<sup>5-7</sup>.

On a general way, with both of the cited techniques it is possible to obtain well-purified nanoparticles ready for characterization experiments or for applications. The first visible difference between the two methods is the cost: the centrifugation requests a centrifuge (and normal laboratory glassware or plastics) while the filtration needs a centrifuge and particular filter units (such as Amicon). In the latter the cost of the filter units is on the order of the hundreds of euros, yielding little expensive the process.

On the other hand the right choice of the purification method stems also from the synthetic process. Indeed nanoparticles are produced both in organic or aqueous media. If the nanostructures are produced in the latter, both filtration and centrifugation could be used. Otherwise only centrifugation (with the right glassware) is exploitable if the particles are dispersed in organic media. This came from the composition of the filters: polypropylene for the tubes and regenerated cellulose for the filters. These materials may suffer the

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Figure 1. A schematic illustration of the two purification processes, centrifugation and filtration. In the first case the surnatant is discarded and the precipitate re-dispersed, in the second the "filtered" is directly re-dispersed. Note that the "centrifugal tube" may be in glass or plastics.

presence of many organic solvents and of certain concentration of molecules, such as reported from the manufacturer.

If the final application of the nanostructures is regarding nanomedicine, biophysics or photochemistry, it is sure that, at a point, the particles would be dispersed in aqueous buffers. Therefore, if the dispersant is aqueous, it is needed to evaluate three other variables: size of the objects, volume of the samples and the surface coatings of nanomaterials.

In the centrifugation process there is "dependence" between the size and the centrifugal-time: briefly, more large are the particles and less time it is needed to precipitate them (and *viceversa*). Thus, for big-size particles (big> 20-nm diameter), 5 to 10 minutes at 10000 rpm are necessary to collect a precipitate, while up to 30-40 minutes could be necessary for smaller one. By filtration, on the other hand, just 3-4 minutes of centrifugation are usually enough to separate the colloid from the solvent. It is useful to know that the pore-size of the filter units is stated in molecular weight (in general KDa), in order to indicate which type of molecules may cut off (as an example, a PEG-12000 polymer can pass through 30K filters but not through 10K ones). The filters are sold with the following pore-size: 3K, 10K, 30K, 50K and 100K. It was observed that while 10K filter cut off nanoparticles with diameter >5nm, the 30K the ones >15nm, and the 100K the ones >30nm.

The volume is another important variable. Indeed by filtration it is possible to purify a maximum of 15 mL of colloidal solution for filter unit, while by centrifugation this value depend from the employed rotor (up to more than 150 mL). Thus for big-volumes of solutions the filtration process could be not the best choice. On the other hand, for small volumes or diluted solutions the filtering process may be useful because it is easier to collect the precipitate.

Furthermore, the surface functionalization of the nanomaterials is a subject to explore. Indeed, while the optical and physical features of nanoparticles are related to the geometry of the structures, the stability and reactivity is linked to the coatings and their covalently linked molecules. Thus, sometimes the centrifugation is a too rough process that leads to irreversible precipitation of the nanoparticles or to the formation of large aggregates. However, the presence on the coatings of some molecules (and in particular some proteins) can leads to a stick of the nanostructures to the cellulose of the filter, causing the complete loss of the sample. In this technical note I intentionally do not take into account dialysis processes by membranes. This because the dialysis may always follow the other purification methods in order to obtain a satisfactory sample.

In summary there is not a best general way to purify nanomaterials, but the best way inherent to your batch. Thus, in order to obtain the best purified sample for the characterizations or the applications with the less possible leakage, a full analysis of the variables here reported is necessary.

#### References.

- 1 Mout, R., Moyano, D. F., Rana, S. & Rotello, V. M. Surface functionalization of nanoparticles for nanomedicine. *Chemical Society Reviews* **41**, 2539-2544 (2012).
- 2 Neely, A. *et al.* Ultrasensitive and highly selective detection of Alzheimer's disease biomarker using two-photon rayleigh scattering properties of gold nanoparticle. *ACS Nano* **3**, 2834-2840, doi:10.1021/nn900813b (2009).
- 3 Aaron, J., Travis, K., Harrison, N. & Sokolov, K. Dynamic Imaging of Molecular Assemblies in Live Cells Based on Nanoparticle Plasmon Resonance Coupling. *Nano Lett*, doi:10.1021/nl9018275 (2009).

- 4 Njoki, P. N., Luo, J., Kamundi, M. M., Lim, S. & Zhong, C. J. Aggregative Growth in the Size-Controlled Growth of Monodispersed Gold Nanoparticles. *Langmuir* 26, 13622-13629, doi:Doi 10.1021/La1019058 (2010).
- 5 Voliani, V., Luin, S., Ricci, F. & Beltram, F. Single-step bifunctional coating for selectively conjugable nanoparticles. *Nanoscale* **2**, 2783-2789, doi:10.1039/c0nr00350f (2010).
- 6 Voliani, V. *et al.* Multiphoton Molecular Photorelease in Click-Chemistry Functionalized Gold Nanoparticles. *SMALL* **7**, 3271-3275, doi:10.1002/smll.201101753 (2011).
- 7 Voliani, V. *et al.* Smart delivery and controlled drug release with gold nanoparticles: new frontiers in nanomedicine. *Recent Patents on Nanomedicine* **2**, 34-44 (2012).

### Selection Rules for Circular Dichroism

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#### **1** Introduction

Optically active molecules exist in two mirror images, the enantiomers. They have identical scalar properties, like energy, but differ in vector properties like electrical and magnetic moments. This is due to a geometrical property, called chirality. Rosenfeld<sup>1</sup> in 1928 identified a characteristic feature, the rotatory strength

 $R_{mn} = \operatorname{Im}\left\{\left\langle 0 \left| \vec{\mu} \right| m \right\rangle \cdot \left\langle m \left| \vec{m} \right| 0 \right\rangle\right\}$ (1)

which is non-zero for chiral molecules. In his theoretical treatment the molecule is placed in a perturbing electromagnetic field which provokes induced and transition moments in addition to a static moment, if that exists.

Optically active materials rotate the plane of polarization of passing linearly polarized light (optical rotatory dispersion, ORD) and absorb left and right circularly polarized light (l-cpl and r- cpl) to a different degree (circular dichroism, CD). In this note the selection rules for

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circular dichroism are derived for circularly polarized light in a straightforward manner by time dependent perturbation theory extended to circularly polarized light.

#### 2 The perturbation of a molecule by light

We follow the standard method of treating the time dependent perturbation of a molecule by light starting from the time dependent Schrödinger equation.<sup>2</sup> A time dependent problem thus requires

$$\Psi(r,t) = \sum_{n} c_{n}(t) \Psi_{n}^{(0)}(r,t)$$
(2)

The absorption of light by a molecule leads to a population of the state m

$$\frac{dc_m}{dt} = \frac{i}{\hbar} \cdot \int \Psi_m^{(0)*} \hat{H}' \Psi_0^{(0)} d\tau$$
(3)

where  $\hat{H}'$  is the perturbation operator of the light wave. This perturbation operator is<sup>2</sup>

$$\hat{H}' = \sum_{j} -\frac{i\hbar e}{2m_{j}} \vec{A}_{j} \cdot grad_{j} = \sum_{j} \frac{e}{2m_{j}} \vec{A}_{j} \cdot \frac{\hbar}{i} \left[ \frac{\partial}{\partial x_{j}} + \frac{\partial}{\partial y_{j}} + \frac{\partial}{\partial z_{j}} \right]$$

$$= \sum_{j} \frac{e}{2m_{j}} \vec{A}_{j} \cdot \vec{p}_{j}$$

$$(4)$$

Here the vector

$$\vec{A}(r,t) = \vec{A}_0(0) \cdot e^{i(\vec{k}\vec{r} - \omega t)}$$
(5)

is called vector potential of the light [Vsm<sup>-1</sup>] at the place r of the electron j and  $\vec{p}_j$  is the electron's momentum [kg m s<sup>-1</sup>= J s m<sup>-1</sup>], both being vectors. The vector potential originally has been

conceived as a purely mathematical construct in physics: The electric and the magnetic fields  $\vec{E}$  and  $\vec{H}$  of an electromagnetic wave are interconnected and the vector potential incorporates the information about both of them. Thus  $\vec{A}$  is appropriate for an electromagnetic wave, the information on the electric field E [Vm<sup>-1</sup>] and the magnetic field B [Vsm<sup>-2</sup>] is brought back by the operators  $(-\partial/\partial t)$  [s<sup>-1</sup>] and the vector operator (*rot*) [m<sup>-1</sup>]<sup>†</sup>

$$\vec{E}(r,t) = -\frac{\partial \vec{A}(r,t)}{\partial t}$$
(6)

and

$$\vec{B}(r,t) = \mu_0 \vec{H}(r,t) = rot \, \vec{A}(r,t) = \vec{\nabla} \times \vec{A}(r,t) \tag{7}$$

where  $\mu_0 = 1.26 \cdot 10^{-6}$  Vs/(Am) is the vacuum permeability constant.

For detecting the chiroptical properties of a molecule a light beam must probe the sense of the twist in the molecule's structure, if any is existent, and thus the fields of the wave must vary at least a bit within the molecular dimensions, to a first approximation linearly. This is taken into account by the development of  $\vec{A}$  in a Taylor series (which is equivalent to developing the exponential in (5))

$$\vec{A}(r) = \vec{A}_0 + \vec{r} \frac{\partial \vec{A}}{\partial \vec{r}} = \vec{A}_0 + \vec{r} \, \vec{\nabla} \cdot \vec{A}_0 \tag{8}$$

<sup>&</sup>lt;sup>†</sup> This is the same approach as the use of the wave function  $\Psi_n$  which contains all the information on the state *n* of a molecular system. The pieces of information are retrieved by means of the energy operator, the angular moment operator etc.

With application of a vector formula<sup>‡</sup> this first order perturbation operator which is appropriate for the derivation of the selection rules for CD, reads

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$$\hat{H}' = \frac{e}{mc} \left[ \sum_{j} \vec{A}_{0}(0) \cdot \vec{p}_{j} + \frac{1}{2} (\vec{\nabla}_{0} \times \vec{A}_{0}(0)) (\vec{r}_{j} \times \vec{p}_{j}) \right] e^{-i\omega t}$$
(9)

When Dirac's bra - ket writing is used for shortening the expressions, (3) becomes with (4) and (9)

$$\frac{dc_{m}}{dt} = \frac{i}{\hbar} \left\langle \Psi_{m}^{(0)} \left| \hat{H}^{\prime} \right| \Psi_{0}^{(0)} \right\rangle = \\
= \frac{i}{\hbar} \left[ \left\langle \Psi_{m}^{(0)} \left| e \sum_{j} \frac{1}{m_{j}} \vec{p}_{j} \right| \Psi_{0}^{(0)} \right\rangle \cdot \vec{A}_{0}(0) + \\
+ \left\langle \Psi_{m}^{(0)} \left| \sum_{j} \frac{e}{2m_{j}} (\vec{r}_{j} \times \vec{p}_{j}) \right| \Psi_{0}^{(0)} \right\rangle \cdot (\vec{\nabla} \times \vec{A})_{0} \right] e^{-i\omega t} \quad (10)$$

$$= \frac{i}{\hbar} \left[ \left\langle \Psi_{m}^{(0)} \left| e \sum_{j} \frac{1}{m_{j}} \vec{p}_{j} \right| \Psi_{0}^{(0)} \right\rangle \cdot \vec{A}_{0}(0) + \\
+ \left\langle \Psi_{m}^{(0)} \left| \sum_{j} \frac{e}{2m_{j}} (\vec{r}_{j} \times \vec{p}_{j}) \right| \Psi_{0}^{(0)} \right\rangle \cdot (\vec{\nabla} \times \vec{A})_{0} \right] e^{i(\omega_{m0} - \omega)t}$$

We now introduce  $(\omega_m - \omega_0 = \omega_{m0} = 2\pi v_{m0})$ . From the textbooks<sup>2</sup> we know the substitution

<sup>‡</sup> from  $\vec{A} \cdot \vec{p} + (\vec{r} \cdot \vec{\nabla}_0)(\vec{A} \cdot \vec{p})$  with

$$(\vec{V}_1 \cdot \vec{V}_2)(\vec{V}_3 \cdot \vec{V}_4) = \frac{1}{2}(\vec{V}_2 \times \vec{V}_3) \cdot (\vec{V}_1 \times \vec{V}_4) + \frac{1}{2}[(\vec{V}_1 \cdot V_2) \cdot (\vec{V}_3 \cdot \vec{V}_4) + (\vec{V}_1 \cdot \vec{V}_3) \cdot (\vec{V}_2 \cdot \vec{V}_4)]$$

<sup>.</sup> The first term is connected to the magnetic dipole moment and is kept; the second term to the electric quadrupole moment, this latter is omitted in this context.

$$\begin{split} \left\langle \psi_{m}^{(0)} \left| e \sum_{j} \frac{1}{m_{j}} \vec{p}_{j} \right| \psi_{n}^{(0)} \right\rangle &= -i\hbar \left\langle \psi_{m}^{(0)} \left| \sum_{j} \frac{e}{m_{j}} \left( \frac{\partial}{\partial x_{j}} + \frac{\partial}{\partial y_{j}} + \frac{\partial}{\partial z_{j}} \right) \right| \psi_{n}^{(0)} \right\rangle \\ &= i \frac{1}{\hbar} (E_{m} - E_{n}) \left[ \left\langle \psi_{m}^{(0)} \left| \sum_{j} ex_{j} \right| \psi_{n}^{(0)} \right\rangle + \left\langle \psi_{m}^{(0)} \left| \sum_{j} ey_{j} \right| \psi_{n}^{(0)} \right\rangle + \left\langle \psi_{m}^{(0)} \left| \sum_{j} ez_{j} \right| \psi_{n}^{(0)} \right\rangle \right] (11) \\ &= i \omega_{mn} \left\langle m \left| \vec{\mu} \right| n \right\rangle \end{split}$$

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which includes the electric dipole moment [Cm]. In the same way

$$\left\langle \psi_{m}^{(0)} \left| \sum_{j} \frac{e}{2m_{j}} (\vec{r}_{j} \times \vec{p}_{j}) \right| \psi_{n}^{(0)} \right\rangle =$$

$$= -i \left\langle \psi_{m}^{(0)} \left| \sum_{j} \frac{e\hbar}{2m_{j}} \left\{ (y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) + (z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) + (x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}) \right\} \right| \psi_{n}^{(0)} \right\rangle (12)$$

$$= -i \left\langle \psi_{m}^{(0)} \left| \vec{m} \right| \psi_{n}^{(0)} \right\rangle$$

The unit of the magnetic dipole moment is  $Cm^2s^{-1}$ . So the time dependence [s<sup>-1</sup>] of the coefficient of state m for population from the ground state 0 is

$$\frac{dc_m}{dt} = \frac{i}{\hbar} \left\langle \Psi_m^{(0)} \left| \hat{H}' \right| \Psi_0^{(0)} \right\rangle$$

$$= \frac{1}{\hbar} \left[ -\omega_{m0} \left\langle m \left| \vec{\mu} \right| 0 \right\rangle \cdot \vec{A}_0(0) + \left\langle m \left| \vec{m} \right| 0 \right\rangle \cdot (\vec{\nabla}_0 \times \vec{A}_0(0)) \right] e^{i(\omega_{m0} - \omega)t}$$
(13)

#### 3 The interaction of circularly polarized light with a molecule

Now it becomes useful to unravel the vector potential. As CD only becomes evident in the interaction of circularly polarized light with chiral molecules it is necessary to consider the components of the electric and magnetic fields in detail.

Circular polarization of a wave traveling in z direction may be understood by the interference of two waves, one polarized in x and one polarized in y direction with equal amplitudes ( $E_{0z} = E_{0y} = E_{0x}$ ) but with a phase difference of 90° or -90°. This results in a screw-like rotation of the field vectors. Unfortunately for the *definition* of right and left circularly polarization physicists and chemists formerly took opposite points of view: the physicist looked *in* the direction of wave propagation, the chemist in the *opposite* direction, i.e. in the direction towards the light source. In the SI-system the standpoint of chemists is adopted.

Accordingly l-cpl is represented by Fig.1



**Fig.1** Left circularly polarized light.  $\vec{E}$  as well as  $\vec{H}$  have components in x and y directions

Fig. 1shows only vectors of the electric field. Those of the magnetic field are perpendicular to the electric field vectors and rotate in phase with them. For l-cpl holds: to  $\vec{E}_x$  belongs  $\vec{H}_y$  and to  $\vec{E}_y$  belongs  $-\vec{H}_x$ .

In the complex notation the fields are expressed as

$$E_{x} = E_{0} e^{i(\omega t - k_{z}z)} \qquad E_{y} = E_{0} e^{i(\omega t - k_{z}z + \pi/2)}$$
(14)

As  $e^{i\pi/2} = \cos \pi/2 + i \sin \pi/2 = i$  we have

l-cpl: 
$$\vec{E} = \vec{E}_x + \vec{E}_y = (E_{0x} + iE_{0y})e^{i(\omega t - k_z z)}$$
  
 $\vec{H} = (H_{0y} - iH_{0x})e^{i(\omega t - k_z z)}$  (15)

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r-cpl: 
$$\vec{E} = \vec{E}_x - \vec{E}_y = (E_{0x} - iE_{0y})e^{i(\omega t - k_z z)}$$
  
 $\vec{H} = (H_{0y} + iH_{0x})e^{i(\omega t - k_z z)}$  (16)

Thus insertion of the field components for 1-cpl in (13) leads to

$$\frac{dc_{m}}{dt} = \frac{1}{\hbar} \left[ -\frac{\omega_{m0}}{\omega} \left\langle m \middle| \vec{\mu} \middle| 0 \right\rangle \cdot \left( E_{0_{x}}(0) + i E_{0_{y}}(0) \right) + \right. \\ \left. + \mu_{0} \left\langle m \middle| \vec{m} \middle| 0 \right\rangle \cdot \left( H_{0_{y}}(0) - i H_{0_{x}}(0) \right) \right] e^{i(\omega_{m0} - \omega)t} \\ = \left[ \left\{ -\frac{\omega_{m0}}{\omega\hbar} \left\langle m \middle| \vec{\mu}_{x} \middle| 0 \right\rangle E_{0_{x}}(0) + \mu_{0} \left\langle m \middle| \vec{m}_{x} \middle| 0 \right\rangle \cdot H_{0_{x}}(0) \right\} - \left. - i \left\{ -\frac{\omega_{m0}}{\omega\hbar} \left\langle m \middle| \vec{\mu}_{y} \middle| 0 \right\rangle \cdot E_{0_{y}}(0) + \mu_{0} \left\langle m \middle| \vec{m}_{y} \middle| 0 \right\rangle H_{0_{y}}(0) \right\} \right] \cdot \\ \left. \cdot e^{i(\omega_{m0} - \omega)t} \right] + \left. \left. \left( e^{i(\omega_{m0} - \omega)t} \right) \right\} + \left. \left( e^{i(\omega_{m0} - \omega)t} \right) \right] + \left. \left( e^{i(\omega_{m0} - \omega)t} \right) \right\} + \left. \left( e^{i(\omega_{m0} - \omega)t} \right) \right] + \left. \left( e^{i(\omega_{m0} - \omega)t} \right) \right\} + \left. \left( e^{i(\omega_{m0} - \omega)t}$$

Integration from time 0 to t and substitution of  $\langle m | \vec{\mu}_x | 0 \rangle = \langle \vec{\mu}_x \rangle$ etc. gives for the coefficient of state *m* 

$$c_{m} = \frac{e^{i(\omega_{m0}-\omega)t} - 1}{(\omega_{m0}-\omega)} \frac{1}{\hbar} \left[ \left\{ -\frac{\omega_{m0}}{\omega} \left\langle \vec{\mu}_{x} \right\rangle \cdot E_{0x}(0) + \mu_{0} \left\langle \vec{m}_{x} \right\rangle \cdot H_{0x}(0) \right\} - \frac{1}{(18)} - i \left\{ -\frac{\omega_{m0}}{\omega} \left\langle \vec{\mu}_{y} \right\rangle \cdot E_{0y}(0) \right\} + \mu_{0} \left\langle \vec{m}_{y} \right\rangle \cdot H_{0y}(0) \right\} \right]$$

The population of state *m* as given by the complex square is

$$c_{m}^{*}c_{m} = \frac{1}{\hbar^{2}} \left[ \left\{ \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{y} \right\rangle^{2} E_{0y}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{y} \right\rangle^{2} H_{0y}^{2}(0) - \frac{1}{2} \left\{ \frac{\omega_{m0}}{\omega} + \frac{\omega_{0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{x} \right\rangle^{2} E_{0y}(0) \left\langle \vec{m}_{y} \right\rangle H_{0y}(0) \right\} + \left\{ \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{x} \right\rangle^{2} E_{0x}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{x} \right\rangle^{2} H_{0x}^{2}(0) - \frac{1}{2} \left\{ \frac{\omega_{m0}}{\omega} + \frac{\omega_{0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{x} \right\rangle^{2} \left\langle \vec{m}_{x} \right\rangle E_{0x}(0) H_{0x}(0) \right\} \right] \frac{2 - e^{i(\omega_{m0} - \omega)t} - e^{-i(\omega_{m0} - \omega)t}}{\left(\omega_{m0} - \omega\right)^{2}}$$

$$(19)$$

By rearrangement

$$c_{m}^{*}c_{m} = \frac{1}{\hbar^{2}} \left[ \left\{ \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{y} \right\rangle^{2} E_{0y}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{y} \right\rangle^{2} H_{0y}^{2}(0) + \right. \\ \left. + \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{x} \right\rangle^{2} E_{0x}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{x} \right\rangle^{2} H_{0x}^{2}(0) \right\} - \\ \left. - 2 \frac{\omega_{m0}}{\omega} \mu_{0} \left\{ \left\langle \vec{\mu}_{y} \right\rangle \cdot \left\langle \vec{m}_{y} \right\rangle E_{0y}(0) H_{0y}(0) + \right. \\ \left. + \left\langle \vec{\mu}_{x} \right\rangle \cdot \left\langle \vec{m}_{x} \right\rangle E_{0x}(0) H_{0x}(0) \right\} \right] \frac{2 - e^{i(\omega_{m0} - \omega)t} - e^{-i(\omega_{m0} - \omega)t}}{(\omega_{m0} - \omega)^{2}}$$

$$(20)$$

The same procedure for r-cpl gives

$$c_{m}^{*}c_{m} = \frac{1}{\hbar^{2}} \left[ \left\{ \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{y} \right\rangle^{2} E_{0y}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{y} \right\rangle^{2} H_{0y}^{2}(0) + \right. \\ \left. + \frac{\omega_{m0}^{2}}{\omega^{2}} \left\langle \vec{\mu}_{x} \right\rangle^{2} E_{0x}^{2}(0) + \mu_{0}^{2} \left\langle \vec{m}_{x} \right\rangle^{2} H_{0x}^{2}(0) \right\} + \\ \left. + 2 \frac{\omega_{m0}}{\omega} \mu_{0} \left\{ \left\langle \vec{\mu}_{y} \right\rangle \cdot \left\langle \vec{m}_{y} \right\rangle E_{0y}(0) H_{0y}(0) + \right. \right. \right.$$

$$\left. + \left\langle \vec{\mu}_{x} \right\rangle \cdot \left\langle \vec{m}_{x} \right\rangle E_{0x}(0) H_{0x}(0) \right\} \left[ \frac{2 - e^{i(\omega_{m0} - \omega)t} - e^{-i(\omega_{m0} - \omega)t}}{(\omega_{m0} - \omega)^{2}} \right] \right]$$

$$\left. \left( 21 \right) \left( \frac{2 - e^{i(\omega_{m0} - \omega)t} - e^{-i(\omega_{m0} - \omega)t}}{(\omega_{m0} - \omega)^{2}} \right) \right] \left( \frac{2 - e^{i(\omega_{m0} - \omega)t} - e^{-i(\omega_{m0} - \omega)t}}{(\omega_{m0} - \omega)^{2}} \right) \right]$$

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The probability of light absorption finally is found by integration over the bandwidth<sup>2</sup>.

#### 3. Discussion

Inspection of the time-independent part of (21) in square brackets reveals that the total absorption is composed of the two parts in curly brackets. The first curly bracket represents the absorption of nonpolarized light, this absorption is characterized by  $\varepsilon$  and is dominated by the (square of the) electric dipole part. The second bracket represents the special contribution of circular polarization. This contribution,  $\Delta \varepsilon/2$ , is added or subtracted for l-cpl und r-cpl respectively. Accordingly  $\varepsilon_1 = \varepsilon - \Delta \varepsilon/2$  and  $\varepsilon_r = \varepsilon + \Delta \varepsilon/2$ , and consequently  $\varepsilon = (\varepsilon_l + \varepsilon_r)/2$ .

Those terms in the second bracket which stand for the CD contain the dot product of electric and magnetic dipole moment integrals. This means that one only expects a difference of the absorption for lcpl and r-cpl if both the electric and magnetic moments of a molecule are different from zero and if they are not perpendicular, i.e. they both at the same time have a component in the direction of the field components. In isotropic solution the molecules have a statistical distribution of their positions relative to the fields. Therefore the condition for the appearance of CD is tied to an *intramolecular* property:

$$\left\langle m \left| \vec{\mu} \right| 0 \right\rangle \cdot \left\langle m \left| \vec{m} \right| 0 \right\rangle = \left| \left\langle m \left| \vec{\mu} \right| 0 \right\rangle \right| \cdot \left| \left\langle m \left| \vec{m} \right| 0 \right\rangle \right| \cdot \cos \phi_{\vec{\mu}\vec{m}} \neq 0$$
(22)

Consequently, CD can only be observed in molecules whose electric and magnetic moments have the same geometric properties, more general: they must have at least components which belong to the same irreversible representation of the molecular symmetry point group.<sup>3</sup> Only molecules belonging to the pure rotation groups  $C_n$  and  $D_n$ , show this property chirality. These point groups have no center of inversion and no symmetry planes, a molecular requirement which has been found empirically long ago. In group theory the geometrical properties of molecules are collected in character tables of the point groups which usually show in an extra column to which representation the coordinates x,y and z and the rotations  $R_x$ ,  $R_y$  and  $R_z$  belong. The combinations  $x/R_x$ ,  $y/R_y$  or  $z/R_z$  for one representation are necessary and are only found in those pure rotation groups.

The condition (22) is essentially the same condition as that of the Rosenfeld formula.

In the course of the derivation of the expression for the absorption of l-cpl and r-cpl there was no mentioning which of the two enantiomers would be the absorbing molecule. The enantiomers differ in the sign of the angle  $\phi_{mn}$  between the transition moments. So the sign of the total CD spectrum is reverted for the two enantiomers and this has its source in the reversal of the sign of the rotatory strength.

As the directions of the electric and magnetic transition moments in *one enantiomer* may vary in different excited states, there may be and usually are, changes of the sign of CD in one spectrum. (The CD/ORD effects in *one absorption band* are called Cotton-effect.) In the CD spectrum of (+)-Hexahelicene (Fig. 2) the absorption band around 320 nm carries positive CD that around 240 nm negative, and that around 220 nm again positive CD. The CD of the enantiomers is compensated in a 1:1 mixture of the enantiomers, this racemic mixture is optically inactive.

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Fig. 2 Absorption and CD spectra of (+) Hexahelicene

This note presents a straightforward derivation of the selection rules for CD only for dissymmetric electronic systems, the inherently dissymmetric molecules. Examples for such twisted electronic systems are the helicenes, allenes, the atropisomeric biphenyls, twisted dienes, some spiro compounds. These molecules show large (on the scale of optical activity) chiroptical effects. For (+)-hexahelicene  $[\Theta]_{320} = +6 \cdot 10^5$  rad m<sup>2</sup>mol<sup>-1</sup> and  $[\Theta]_{245} = -7 \cdot 10^5$  rad cm<sup>2</sup>dmol<sup>-1</sup>.

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By far the most optically active molecules, however, have not an inherently dissymmetric but a symmetric electronic system, called the chromophore, and a dissymmetric environment. A standard example is 3-methyl-cycolohexanone, where the carbonyl group sees an "asymmetric" C-atom. This environment causes a *time-independent* dissymmetric perturbation of the chromophoric electronic system and thus induces optical activity. The induced activity is much lower than that of inherently dissymmetric chromophores, (+)-3-methylcyclopentanone e.g. shows  $[\Theta]_{310} = 8 \cdot 10^3$  rad cm<sup>2</sup>dmol<sup>-1</sup> in the n $\rightarrow \pi^*$  band, and this is a comparatively large value. The sign of the CD depends on the geometry of the surroundings and thus can be used for structural analysis for which the famous empirical sector

rules were set up. In order to understand them it is necessary to include time-independent perturbation theory for the dissymmetric perturbation of chromophores. This causes a reduction of symmetry of the wave function of the symmetric chromophore and mixing in states with non-zero rotatory strength. The source of the dissymmetric perturbing field may be seen in point charges fixed at the atoms of the environment (incomplete shielding of nuclear charges)<sup>4</sup>, isotropically polarizable<sup>5</sup> or anisotropically polarizable<sup>6</sup> perturbation centers there. For the carbonyl group in the first case a quadrant rule results, in the second case an octant rule and in the third case sector rules with bent boundaries. So the many empirical rules are rationalized by a superposition of these three cases.

<sup>&</sup>lt;sup>1</sup> L.Rosenfeld, Quantenmechanische Theorie der natürlichen optischen Aktivität von Flüssigkeiten und Gasen, Z. Physik (1928), 52, 161-174

<sup>&</sup>lt;sup>2</sup> J.E. Walter, H. Eyring, G.E. Kimball , *Quantum Chemistry*, Wiley, New York , London, 1944, Chapter VIII.

<sup>&</sup>lt;sup>3</sup> For group theory see e.g. F.A. Cotton, *Chemical Applications of Group theory*, Wiley-Interscience, New York, 1964

<sup>&</sup>lt;sup>4</sup> J.A. Schellman, *Symmetry Rules for Optical Rotation*, J. Chem. Phys. (1956), 44, 55-63

<sup>&</sup>lt;sup>5</sup> J.G. Kirkwood, On the Theory of Optical Rotatory Power, J.Chem.Phys. (1937), 6, 479-491

<sup>&</sup>lt;sup>6</sup> E.G. Höhn, O.E. Weigang, *Electron Correlation Models for Optical Activity*, J.Chem.Phys. (1968), 48, 1127-1137

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### PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



### **CONFERENCE REPORTS**

### Central European Conference on Photochemistry (CECP) 2012

From Sunday, February 5 to Thursday, February 9, 2012, 113 photochemists from 16 different countries came together to share their results and experiences at the Congress Centre of Bad Hofgastein/Austria. It was a wonderful atmosphere and all participants really enjoyed the meeting. The scientific organization has been done by the international scientific committee: Dominik Wöll, Konstanz, Germany, Fred Brouwer, Amsterdam, The Netherlands, Jacques E. Moser, Lausanne, Switzerland, Sebastiano Campagna, Messina, Italy, Ottó Horváth, Veszprém, Hungary, Esther Oliveros, Toulouse, France, and Tomas Polivka, Ceske Budejovice, Czech Republic. Unfortunately Sebastiano Campagna could not attend the meeting due to heavy snow fall in Italy on Sunday, but he did a good job as chairman during preparation of the conference. The conference started on Sunday with the come



Figure 1. Plenary speakers of CECP 2012, from left to right Scandola, van Grondelle, Heilemann, Biczók (first row), Lacombe, Nüesch, Krees, and Tausch (second row).

together including a buffet and an opening lecture.

From Monday to Wednesday there were two sessions per day with one plenary lecture in each session (6 plenary lectures and an experimental lecture of Michael Tausch from Wuppertal/Germany, presented together with Simone Krees), as well as short talks (24 oral presentations), and a poster session every evening (74 poster presentations). Plenary lectures have been given by Franco Scandola, Ferrara (I) on Supramolecular strategies towards functional units of artificial photosynthesis, Rienk van Grondelle, Amsterdam (NL), on Photosynthetic Light-Harvesting: Lessons From Nature, Mike Heilemann, Würzburg (D), on Imaging cellular structures with near-molecular resolution using photoswitchable fluorophores, László Biczók, Budapset (H) on Photochemistry and photophysics of alkaloids and their supramolecular complexes, Sylvie Lacombe, Pau (F), on Photocatalysis and photosensitization as green process for the treatment of VOCs and foul odours: from material chemistry to the detection of reactive species, and Frank Nüesch, Dübendorf (CH), on Electronic processes at organic optoelectronic device interfaces.

In order to keep the scientific level of the meeting on a internationally high one the scientific committee selected 6 plenary lectures (out of 18 suggestions) and 24 (out of 44 applications) short talks. All poster applications were accepted after checking by the local committee. All travel grant applications (altogether 10) could be accepted for funding. Additional funding from EPA (via Eric Vauthey) and GDCh (via Dominik Wöll) for invited speakers is also gratefully acknowledged. The local organizing committee has been formed by: Stephan Landgraf (local coordinator from EPA Austria), Sabine Richert, Alexander Wankmüller, and Anna-Maria Wernbacher. Additional help from Heidi Schmitt (also for the conference photos) is also gratefully acknowledged. The variety of different accommodations is available in Bad Hofgastein from private rooms up to hotels with a high comfort. Even during high season rooms are available in appropriate number if booked early enough. Contact person for accommodation: Monika Neu, tourist office. Official web site of the meeting is www.cecp.at

The key idea of the **CECP** meeting is to bring together young and experienced photochemists from all photochemical fields. Therefore everything was done to remove all hindrance to join the meeting. Additionally the evening should be undisturbed by the EPA Newsletter

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dinner. So, four evening buffets were organized for all participants. The costs were included in the conference fee. So for students the conference itself has been free of charge. Young researchers up to 4 years after PhD, all attendees from Eastern European countries, and retired researchers could join for a reduced fee, too. The system behind this could be seen in the budget plan of the meeting (Fig. 2). For the first time a reduced fee for EPA members has been offered (2/3 of the annual member fee). For CECP 2014 held in second week of February, 2014, in Bad Hofgastein a significant increase of the fees has to be accepted to compensate inflation.

The location of the Conference Centre of Bad Hofgastein allows a perfect access to physical activities during the afternoon break. Downhill and cross-country skiing, as well as the thermal bath and spa, offer a variety of possibilities to enjoy the region or to relax. Together with the scientific program an ideal combination is present at this place.



Figure 2. Congress centre of Bad Hofgastein. Photo from 2012.

Finally 127 persons registered for the meeting till the beginning of the conference. Since 2006 there have been some fluctuation in the distribution of participants. As shown in Fig 3. the regular



Figure 3. Participants of CECP 2012 in comparison to former CECP meetings.

participants are 39 to 47 %, the East Europeans, young and retired researchers are 20 to 34 %, and 38 to 53 % are students (PhD not completed). Most of the participants come from Germany, but there also significant attendance from France, Switzerland, Russia, Sweden, Italy, and Czech Republic (with 5 participants and more).

All travel grant applications have been accepted by the Governor of Salzburg or the local coordinator. 12 attendees have been supported by this procedure.

See you again in 2014.

#### **CECP 2012** Awards for Young Scientists

Additionally there are two prices for young scientists to encourage them to present their best results at the CECP meeting. All oral and poster presentations have been evaluated by the international scientific committee. Both prices have been awarded by Günter Grampp, Graz at the end of the meeting at the closing ceremony.

CECP 2012 Award for best oral presentation: (O19), David **Bléger**, Berlin, D, "*Macromolecular Accordions*"



CECP 2012 Award for best poster presentation: (P3), Franziska **Graupner**, Munich, D, "Formation of DNA photolesions resolved by transient IR-spectroscopy and time-resolved fluorescence spectroscopy"



Table 1. Former CECP awards.

Year	Award for best	Award for best
	oral presentation	poster presentation
2006	David <b>Bailey</b> , Bremen/D	Katja <b>Draxler</b> , Konstanz/D
2008	Dominik <b>Wöll</b> , Konstanz/D	David Carteau, Bordeaux/F
2010	Simone <b>Draxler</b> , Munich/D	Sabine <b>Richert</b> , Graz/A

Stephan Landgraf Graz University of Technology, Austria EPA Newsletter

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### INVITATIONS

### Photochemistry Summer School 2012 "Photochemistry, Fundamentals and Applications"

September 15-19, 2012, Wijk aan Zee, The Netherlands

It is our pleasure to announce the 4th Photochemistry Summer School 2012, an advanced course covering fundamentals and applications of photochemistry. This School will be from September 15-19, 2012 in Wijk aan Zee (The Netherlands) and is organized by the Holland Research School of Molecular Chemistry under the auspices of the European Photochemistry Association (EPA). This post-graduate school is intended for PhD students and other interested scientists who are active in the field of photochemistry in the broadest sense, or make use of photochemical or photophysical methods in their research work. The specialized lectures by international experts will be preceded by a short (optional) recapitulation of the basic aspects of molecular photochemistry and photophysics.

The lecturers will be:

- Céline Frochot (Nancy, France; photodynamic therapy)

- Rienk van Grondelle (Amsterdam, NL; photosynthesis)

- A. Prasanna de Silva (Belfast, UK; fluorescent sensors)

- Michel Orrit (Leiden, NL; single molecules and particles)

- Adalgisa Sinicropi (Siena, Italy; computational photochemistry)

- Sander Woutersen (Amsterdam, NL; time-resolved IR spectroscopy & molecular motion)

Registration is open for PhD-students, postdoctoral students and industrial scientists.

Check the report in the EPA Newsletter about the previous school. This one will be as interesting and stimulating!

http://www.photochemistry.eu/newsletter/EPA\_Newsletter\_De cember\_2008.pdf

For more information and registration see http://www.hrsmc.nl/drupal/photochemistryschool/

## **MEMBERSHIP APPLICATION FORM**



## EUROPEAN PHOTOCHEMISTRY ASSOCIATION 2011 MEMBERSHIP RENEWAL/APPLICATION FORM

Please complete the form and send it to the Treasurer by mail or fax (do not use e-mail for security reasons!): Dr. SIV40 Canonica Eawag, W+T Dept. Ueberlandstrasse 133, P.O. Box 611, CH-8600 Dübendorf, Switzerland (Fax +41 44 823 5210)

I wish to renew/apply for membership of the European Photochemistry Association (EPA)

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If you are applying for a new membership or if your contact details have changed, please fill in the following section: Address: (Please use your institutional address)

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Membership fees for 2011 in EUR (please check one box) The membership fee includes electronic subscription to the EPA official journal *Photochemical & Photobiological Sciences*, the EPA Newsletter and reduced conference fees.

regular	□ 30 EUR
student*	<ul> <li>15 EUR</li> <li>* p lease supp ly attestation</li> </ul>

For countries with economic difficulties, a reduced fee of 15 EUR can excepti be applied on request (only upon written approval by the Treasurer). nallv

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