

ASP NEWS



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IN THIS ISSUE

Virtual Poster Symposium.....	1
Meet a Photobiologist.....	1
Photodynamic Therapy	2
Photochemistry Correspondence.....	3
Photochemistry: Pick a Color.....	4
Photobiology: Glowing Mushrooms.....	6
Upcoming Photobiology Events.....	7

Inaugural Virtual Poster Symposium

The inaugural ASP Virtual Poster Symposium is now officially underway with the submission of abstract deadline now passed.

A number of abstracts on a range of photobiological topics were received and accepted, with judges looking forward to seeing the finished posters. All applicants should now have been notified if their abstract was accepted. If any applicant has not received a decision, they are encouraged to contact joanna.turner@usq.edu.au for further information.

Accepted applicants will soon be provided with the judging criteria for their poster and optional video, as well as the guidelines for selecting the “crowd voted” prizes – otherwise known as the People’s prizes.

All information regarding the Virtual Poster Symposium is available at the ASP website: <http://photobiology.org/virtual2015/>.

-Joanna Turner, PhD

Meet a Photobiologist

Jean Cadet

PhD, Grenoble University

Photochemistry and Photobiology Editor-in-Chief



Q: *What area of photobiology are you researching?*

A: I have been working for a long time with photobiology and photochemistry of DNA. Ultraviolet photosensitization is a complex process that I have been trying to understand.

Q: *How did you become the editor of Photochemistry and Photobiology?*

A: I became an associate editor towards the end of the 1990s. I was invited at the beginning of the 2000s to become editor-in-chief by Tito Scaiano and some others, but I initially declined. They were persistent though and I finally accepted the job in 2009. My first six year term ended last year and I am on my second term now.

Q: *That must take a lot of your time.*

A: Particularly when I first started, I had to learn a whole new operation. It does take a lot of time and I have worked on the journal basically every single day

since I started. It is something that is always on my mind and there is always work to do.

Q: How many articles do you process?

A: It varies, but the average is around 500-600 submissions per year. Some of those are outright rejected. That is more than one or two per day.

Q: Would you like to increase that number of submissions?

A: Absolutely. If we could get slightly more high quality submissions, it would greatly improve the impact and reputation of the journal. This is actually a serious issue. Currently, the number of submissions to the journal and its impact factor are doing alright, but we do not want to these to decline by any amount.

Q: How can ASP members help?

A: It is a journal of an American society yet only about 10-15 % of the articles are coming from North America. We need to get more submissions from ASP members. I am not asking members submit every article to Photochemistry and Photobiology, but if members made an effort to keep the journal in mind when submitting their work and try to contribute an article every 2-3 year, that would help the journal a lot. Working with Wiley, we have developed a streamlined peer review process for creating respectable and high quality articles. It is an excellent place to communicate photobiology research.

-We reached Jean Cadet by phone in Sherbrooke, Quebec



We need YOU!

Please submit content (science highlights, suggested links, personal stories, etc) to ASP News.
Email: jflovell@buffalo.edu

Photodynamic Therapy: From bench to bedside by a non-PDT scientist

I remember the day very well. Sunny, warm late afternoon just right for an after work drink on my backyard deck. I had just uncorked a very nice Australian red, and sat down for my first sip. Around my fence came my next door neighbor, John who had been walking his Dobermans and I invited him to come up and join me. As we sat sipping away, I asked him how his mother Marge was doing. Her voice had developed what first sounded like a raspy sore throat some time earlier, actually some weeks earlier, and which sounded to me as though it was not getting better. In fact, her voice seemed to be getting weaker and weaker over time. This led me to think she was going to lose it altogether. John began to explain that despite several attempts at removing some “growths” on her vocal cords, nothing was working. As John described it, she had several operations, had to undergo a great deal of trauma in her mouth and throat with excessive bleeding and pain with each surgery and, psychologically was getting very depressed thinking she was going to lose her voice. Indeed, her whole family was beginning to worry a great deal not knowing what was happening. Marge, is a gregarious, lovely lady of Greek-American extraction who loved my own Greek-style grilled lamb and I her cooking. The possible loss of her voice was very disturbing.

The more John described her symptoms, such as the growths were not healing after several treatment attempts, and progressing without letup, the more I began to think of PDT as an alternative approach. It sounded to me that Marge might be a good candidate for this type of therapy and I began to explain to John what PDT was having had my first introduction many years earlier while PDT was largely still in the experimental stage but showing promise.

Here is how it happened: Years earlier, I had received in the mail a grant application to review from the American Cancer Society. It was submitted by someone I had never heard of and about an experimental approach I was unfamiliar with. Not having heard of either the grant submitter, the late Dr. Hariharan, or the process, photodynamic therapy using hematoporphyrin derivative (HPD) as a sensitizer and red light as the photon source, but rather curious to find out what it was about, I agreed to review the grant. If it

was something I could not evaluate I would return the application immediately with an apology. After reviewing the proposal my thinking was that while the experimental approach was new to me, the potential of this approach was highly significant. Following my further review of this area, using a photosensitizer and red light, both of which could be directed to biological target e.g. one deep inside a brain or a breast, I sensed that if this approach could successfully demonstrate its efficacy this could someday turn out to be a big step forward in attacking those intractable tumors so difficult to treat in more conventional ways. Indeed, earlier studies at Roswell Park by Thomas Dougherty and colleagues showed very promising results. The more I read the more I became excited about this approach and its potential. I immediately sent back to ACS a very positive evaluation explaining that while it was experimental, it was well worth the effort to fund.

After describing all of this to John, I gave him Dr. Rox Anderson's email. I had known Rox for several years when he was working as an MIT physicist on lasers at the Wellman Center in the MIT-Harvard medical program before going on to Dermatology. Rox is currently Harvard Medical School Professor in dermatology and Director of The Wellman Center for Photomedicine. Rox, I maintained would be a great contact and might know someone in the DC area specializing in PDT. It would be definitely worth a try. John, himself an MIT graduate in Architecture, knew both universities and the Boston area very well and agreed. We finished our wine and John left thanking me for this information. Nothing more of this conversation transpired between us until some months later.

By chance one day I saw Marge and asked after her and was amazed to hear her speak. Her voice had clearly improved. She told me John had mentioned my conversation. They had followed up and eventually got a referral to a local physician whom she contacted and with whom she had several sessions with her new "light therapy" here in the DC area. Marge was very happy with the results and thanked me over and over about her new therapy.

Over the intervening years, PDT has proven itself the formidable opponent to some of those recalcitrant tumors I had hoped it might be. And while my interest in mechanism lay in other areas of photobiology and

photochemistry, I am, nonetheless, really pleased to see this field advance both in the lab and in the clinic.

Although I have never been involved in PDT therapy, I told myself, let's chalk up one more success for science! How thrilling it was for me, as a scientist in another field, to be involved in a small way to be of help to a neighbor. To this day, Marge and our families continue to share good wine and excellent grilled lamb among other Greek and Italian cuisine.

EPILOGUE: While at the ASP meeting in Montreal in 2012 I ran into Dr. Tayyaba Hasan. Tayyaba also is at the Wellman Center for Photomedicine and is a Professor of Dermatology, Harvard Medical School. Tayyaba is, of course, an internationally recognized and very well-regarded scientist as a PDT expert. I explained my story about John's mom and asked her about an email John sent to Rox Anderson about trying to find a PDT therapy specialist in the Washington DC area a couple of years earlier. Tayyaba was, indeed, familiar with this story and relayed the following to me: John attempted to contact Rox Anderson by email. Rox, however, was away and the email got forwarded to her. She in turn followed up on it and eventually the name of a physician was forwarded to John here in DC who had experience with a type of phototherapy that was felt could lend itself to Marge's problem. It did!

I take this opportunity to thank the real PDT specialists who generously got involved and significantly helped in saving a woman's voice. I am very happy to report 5 years later Marge's voice is fully recovered.

-Ed De Fabo, PhD

Correspondence: Two-photon photoisomerization of rhodopsin?

I read with some interest and concern the press release about the paper by Palczewski, et al. on seeing in the infrared that appeared in ASP News that just appeared. Since my group did very extensive studies in the early 1970s (JOSA, 1973) on infrared vision out to 1064 nm (attached), I was interested. After I obtained a copy of their paper, I went back and studied my paper along with the recent PNAS paper on a couple of points. I think that while their findings are interesting, they are

drawing conclusions that are far broader than they should. They did not use a CW laser, but a 200-fs, 75 MHz laser source (with duty cycle of only 1.5×10^{-5} , so non-linear effects are not surprising. We saw only red when we stared into pure CW IR lasers above threshold for seeing, and we saw 532-nm, (color matched green) with Q-switched lasers above threshold. At the visual threshold for the q-switched pulsed laser, we did not always see green, but occasionally white, which Wolbarsht pointed out was well known that color identification of a point source at near threshold is difficult, since it is probably just one cone or a couple photoreceptors - indeed maybe rods for 2-photon. In my view, they made an inherent and incorrect assumption that the 75-MHz pulse train was CW even if for retinal exposures we treat it as the same as CW for safety limits. Their average power entering their eyes as 1 mW actually has peak powers of 66 W, and in a minimal effective spot size of 25 μm would produce a retinal irradiance of more than 13 MW/cm²! Non-linear effects would certainly be expected. Note that we saw SHG at 1064 but not at 694.3 nm (attached), which is consistent with their finding. We interpreted this as showing the extremely low SHG efficiency of the effect which we visually detected at 1060 and 1064 nm. I wonder if they actually read our paper? Chuckle!

-David Sliney, PhD

Photochemistry: Pick a color, any color

In 2005, scientists studying tiny sac-like creatures called sea squirts found bacteria containing two types of chlorophyll (*a* and *b*) in cavities inside the squirts' tissues. These two pigments were soaking up most of the sunlight — the violets, indigos, blues, green, yellows and oranges.

All that filtered through the squirts was deep red light. So the scientists were surprised to discover a film of photosynthesizing microbes on the underside of the squirts as well. They turned out to be full of chlorophyll *d*, a rare variant of the chlorophyll molecule that absorbs near-infrared light.

By tinkering with the chlorophyll molecule, evolution had managed to contrive a version that soaks up the last bit of sunlight, adapting the bacteria to life in perpetual shade.

It is an astonishing feat, but one achieved by nature's traditional method of trial and error. A team of three chemists who study pigments like chlorophyll aspire to a different level of mastery, understanding how the pigments work from first principles and well enough to manipulate their light absorption at will.

The three are Jonathan Lindsey, PhD, the Glaxo Professor of Chemistry at North Carolina State University; David Bocian, PhD, distinguished professor of chemistry at the University of California-Riverside; and Dewey Holten, PhD, professor of chemistry in Arts & Sciences at Washington University in St. Louis.

They began with a bang: in a set of publications in Photochemistry and Photobiology, they described the counter-intuitive ways the chlorophyll molecule's chemical structure sometimes alters the color of light it absorbs.

In two recent articles in the Journal of Physical Chemistry B, they describe how they used that knowledge to push the absorption of pigments into the less-explored territory of the far reds and near infrareds.

By making the molecules from scratch and studying their properties, "we have been able to understand at the most fundamental level why chlorophyll-like molecules have the colors they do, how nature tuned those colors, and how we can tune them for our own research purposes," Holten said.

Solving the mystery of chlorophylls *a* and *b*: The pigments that make grass green and some bacteria purple all have rings of carbon (and nitrogen) atoms alternately linked by single or double bonds.

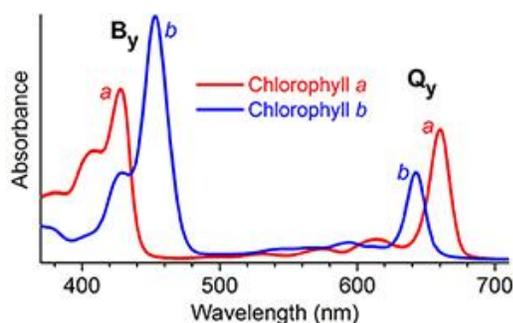
The alternating bonds create what is called a conjugated system, where the outermost electrons on the atoms are delocalized and inhabit orbitals (regions of electron density) that are associated with the molecule as a whole rather than with individual atoms.

A photon with just the right amount of energy (color) will promote one or more electrons to higher energy molecular orbitals. The energy difference between the molecular states, which is related to the energy spacing between the orbitals involved, determines the color of light absorbed.

Which color this is depends on the structure of the ring, but also on the chemical groups attached to it. These groups, called substituents, change the symmetry, electron-density shapes and energies of the molecular orbitals. In the case of the chlorophylls, one of the most important substituents for tuning color is a formyl group (HC=O).

But there's a bit of a mystery here. The addition of the formyl group to the seventh carbon in chlorophyll *b* creates absorption bands that lie inside the main absorption bands of

chlorophyll a. But the formyl group linked to the third carbon in chlorophyll d and at the second carbon in chlorophyll f shifts absorption to the red, outside the chlorophyll a bands.



Why do the peaks in chlorophyll b's light absorption lie inside those of chlorophyll a?

Why does formyl substitution at the seventh carbon have such different consequences than its substitution at the third or second carbon?

To find out, Lindsey synthesized many different versions of chlorophylls from simple to more complex. This menagerie of molecules included ones that had a formyl group at the key third and seventh carbons together with a parent bearing no substituents at all. He then shipped these synthetic molecules to Bocian's and Holten's labs for analysis using spectroscopic and theoretical methods.

"One of the first things we did was molecular-orbital calculations in which we walked the formyl group around the ring, attaching it to each of the carbons in succession to see what would happen to the molecular orbitals," Bocian said.

When light absorption promotes electrons among these orbitals, it causes a net change in electron density along either the x or y molecular axes, or both. "Four possible electron promotions should give four absorption bands, although the extent of mixing between them also influences the spectra," Holten said. The two absorption bands in the violet/blue region of the spectrum are called B_y and B_x , a weak band in the green-yellow region is called Q_x and the last band, in the red or near infrared, is called Q_y .

Bocian's calculations showed that the formyl on the seventh carbon of chlorophyll b draws electrons away from the core of the molecule along the molecular x axis. "It's off-axis," Bocian said. "It pulls on the orbitals in a way that weakens the Q_y absorbance and shifts it to shorter wavelengths."

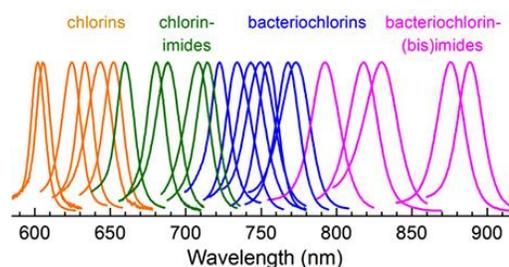
One of the recurring themes of the chemists' work is that as Q_y moves to longer wavelengths and gets stronger, its partner B_y moves to shorter wavelengths and gets weaker. This coupling between partner states explains why

chlorophyll b's absorption bands lie within those of chlorophyll a.

The work was published in the online edition of Photochemistry and Photobiology on January 12, 2015. "That one paper is the culmination of a decade of work by our three groups to understand the interplay of the nature of the conjugated group and its position," Lindsey said.

Having learned as much as they could about the native pigments, the group set out to design new pigments that would absorb parts of the spectrum less utilized or untouched by the native chlorophylls of plants or the bacteriochlorophylls used by photosynthetic bacteria.

Their first goal was to fill the gap between the longest-wavelength absorption they had achieved with chlorins and the shortest-wavelength they had achieved with bacteriochlorins. By positioning several conjugated groups along the y axis of a chlorin, they got the biggest red shifts for chlorins they have achieved to date.



Using their new-found knowledge of the link between structure and absorption, the chemists were able to synthesize molecules that filled a hole in the absorption spectrum of native pigments (the chlorin-imides) and extended absorption deeper into the infrared (the bacteriochlorin-(bis)imides).

The work on the new pigments, called chlorin-imides, was published online in The Journal of Physical Chemistry B on January 14, 2015.

Next they tried to push the absorption wavelengths of the bacteriochlorins as far into the near infrared as they could. "To do so we put as much conjugation as we could along the y axis," Lindsey said. Some of the resulting molecules, called bacteriochlorin-bismides, had peak absorption at about 900 nanometers, far deeper in the near-infrared part of the spectrum than the native bacteriochlorins.

Most recently the chemists have pushed even deeper into the infrared by loading the y axis of a bacteriochlorin with additional chemical groups. As a proof of principle they also showed that if groups were attached to the x axis, the absorption shifted in the other direction.

To test their theory, they also put conjugated groups on the x axis. To their delight, the absorption of these molecules shifted to shorter wavelengths.

“That’s the same thing chlorophyll b does,” Lindsey said. “It puts the conjugated group on the x axis. So there’s a scientific commonality that is very gratifying.”

“If you give us a chemical structure of a chlorophyll-like or bacteriochlorophyll-like molecule,” Holten said, “we can pop it into Gouterman’s four-orbital model and tell you which colors of light it will absorb.

“Or, flip it the other way,” he said. “If you come to us and say we’d like to have a molecule of this type that is going to absorb a narrow band of light centered on some particular red or near-infrared wavelength, say 750 nanometers, we could tell you how to synthesize one that will give the spectrum you want.”

-source: UCSB

Photobiology: Some mushrooms glow, and here's why

Did you know that there are mushrooms that actually glow? Aristotle was aware of this intriguing fact more than 2,000 years ago. He also was the first person to ask a simple question in print: Why? Now, researchers reporting in the Cell Press journal *Current Biology* on March 19 finally have a good answer. The light emitted from those fungi attracts the attention of insects, including beetles, flies, wasps, and ants. Those insect visitors are apparently good for the fungi because they spread the fungal spores around.

The new study also shows that the mushrooms' bioluminescence is under the control of the circadian clock. In fact, it was that discovery that led the researchers to suspect that the mushrooms' light must serve some useful purpose.

"Regulation implies an adaptive function for bioluminescence," explains Jay Dunlap of Dartmouth's Geisel School of Medicine.

"It appears that fungi make light so they are noticed by insects who can help the fungus colonize new habitats," says Cassius Stevani of Brazil's Instituto de Química-Universidade de São Paulo. The circadian control of bioluminescence makes the process more efficient.

There are many examples of living things that generate light in various ways. Among bioluminescent organisms, fungi are the most rare and least well understood. Only 71 of more than 100,000 described fungal species produce green light in a biochemical process that requires oxygen and energy. Researchers had believed in most cases that fungi produce light around the clock, suggesting that perhaps it was a simple, if expensive, metabolic byproduct.

The new work led by Dunlap and Stevani suggests that just isn't so, at least not in the case of *Neonothopanus gardneri*, one of the biggest and brightest of bioluminescent mushrooms. *N. gardneri* is also called "flor de coco," meaning coconut flower, by locals in Brazil, where the mushroom can be found attached to leaves at the base of young palm trees in coconut forests.

The researchers found that the mushrooms' glow is under the control of a temperature-compensated circadian clock. They suggest that this level of control probably helps the mushrooms save energy by turning on the light only when it's easy to see.

To find out what that green glow might do for the mushrooms, the researchers made sticky, fake mushrooms out of acrylic resin and lit some from the inside with green LED lights. When those pretend fungi were placed in the forest where the real bioluminescent mushrooms are found, the ones that were lit led many more staphilinid rove beetles, as well as flies, wasps, ants, and "true bugs," to get stuck than did sticky dark mushrooms.

Dunlap says they are interested in identifying the genes responsible for the mushrooms' bioluminescence and exploring their interaction with the circadian clock that controls them. They are also using infrared cameras to watch the interaction between *N. gardneri* mushrooms and arthropods, especially larger ones, more closely.

The findings are not only cool, they are also important in understanding how mushrooms are dispersed in the environment, the researchers say. That's key because mushrooms such as *N. gardneri* play an important role in the forest ecosystem.

"Without them, cellulose would be stuck in its form, which would impact the whole carbon cycle on Earth," Stevani says. "I dare to say that life on Earth depends on organisms like these."

Some fungi in the group known as basidiomycetes, including two bioluminescent mushrooms, are also parasites of coffee and pine trees. As a result, Stevani says, "it is very important to know how basidiomycetes grow and consequently how they spread their spores."

-source: Cell Press



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Upcoming Photobiology Events

ASP 38: May 21-25, 2016, Tampa Bay

The time and place has been set! Mark your calendar and plan on joining ASP for the next conference.



22-26 May, 2015

International Photodynamic Association Congress
Rio de Janeiro, Brazil

<http://meetings.cepof.ifsc.usp.br/ipa-spie-2015>

June 28-July 3, 2015

The 27th International Conference on Photochemistry
Jeju, Korea

<http://www.icp2015.org/>



9th-11th September, 2015

Japanese Photochemistry Association. Annual Meeting

Osaka, Japan

<http://photochemistry.jp/2015/en/index.html>

Other Event Calendars

SPIE Events: <http://spie.org/x1375.xml>

Plant Biology Events: <http://aspb.org/calendar>

Chemistry Events: <http://www.chemistry.org>

Gordon Conferences: <http://www.grc.org>

Nature Events Directory:

www.nature.com/natureevents/science