Illuminating the Photochemistry of Renaissance Pigments

Ultrafast Spectroscopy of Hydroxyanthraquinones

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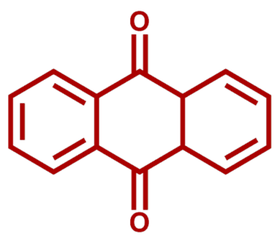
The Fugitives

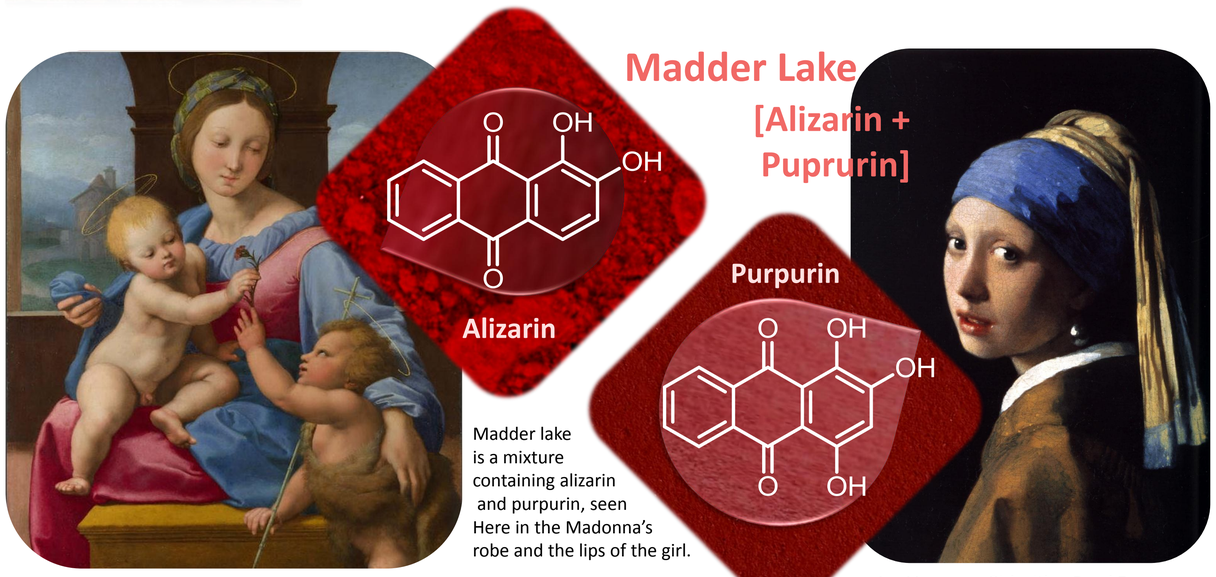
Naturally occurring 9,10-anthraquinone derivatives have been used as red dyes and pigments for nearly 3000 years,[1] notably during the Renaissance. The lakes of these anthraquinones (the natural dye mordanted with alum) are notoriously 'fugitive' - vulnerable to light.[2]

Rubia tinctorum

Madder lake is a mixture of anthraquinones extracted from the root of *Rubia tinctorum.* Alizarin (1,2-Dihydroxy-9,10-anthraquinone) and purpurin (1,2,4-Trihydroxy-9,10-anthraquinone) are principal components of this fugitive mixture, but the exact mechanism of their photodegradation is not well understood.



9,10-anthraquinone



Rafaello Santi (Raphael): *The Garvagh Madonna*

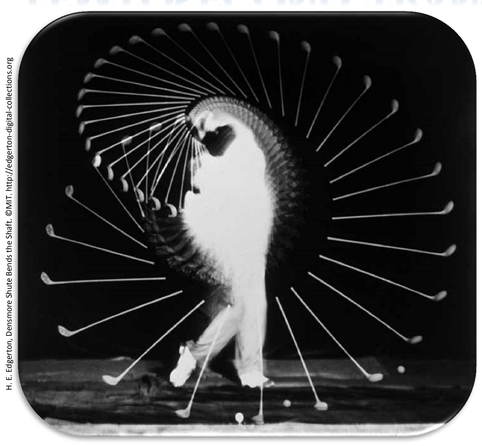
Madder lake is a mixture containing alizarin and purpurin, seen Here in the Madonna's robe and the lips of the girl.

Jan Vermeer: *Girl with a Pearl Earring*

The TrA studies presented here represent the first femtosecond time-resolved spectroscopy of alizarin and purpurin[3], showing that even small structural differences can have a large impact upon the molecule's photodynamics.

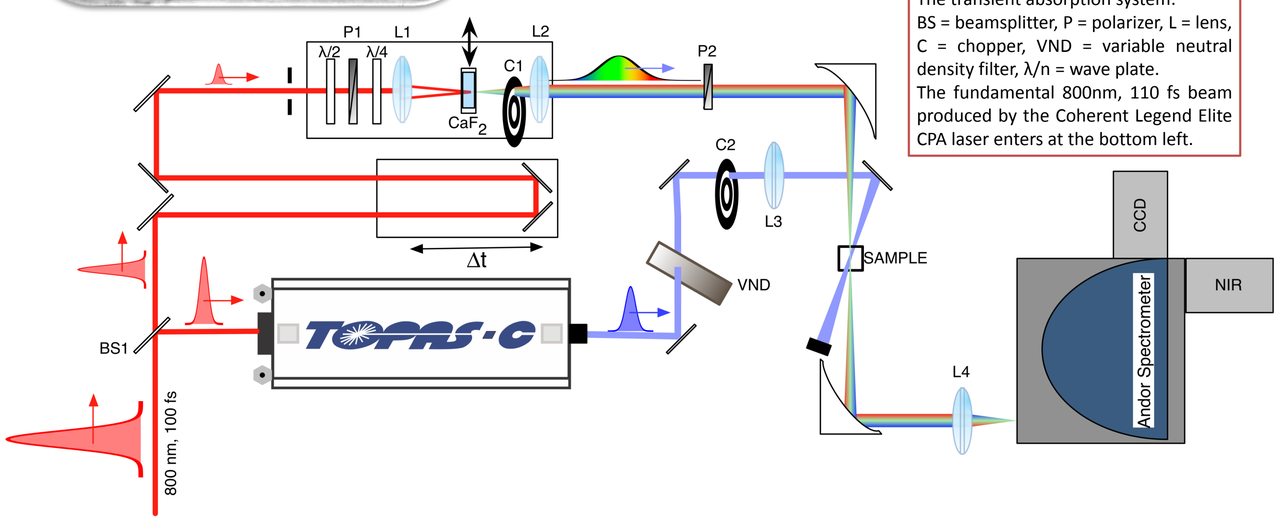
Experimental Methods

Femtosecond Transient Absorption Spectroscopy



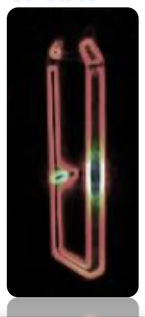
1. The molecule is excited with a ~ 110 femtosecond, single colour pulse (*pump*).
2. After a given time delay (Δt), a broadband (*probe*) 'snapshot' absorption spectrum is measured. Many of these in sequence give the time-resolved spectrum.

This can be thought of as molecular multiflash photography – like the golf player, the electrons/nuclei are moving through both space and time, and the combination of many spectra taken at different times allows us to follow this movement as it occurs.



The transient absorption system:
BS = beamsplitter, P = polarizer, L = lens, C = chopper, VND = variable neutral density filter, λ/n = wave plate.
The fundamental 800nm, 110 fs beam produced by the Coherent Legend Elite CPA laser enters at the bottom left.

Sample Composition and Experimental Conditions



Sample composition: Anthraquinone (Alizarin or Purpurin) in acetonitrile (MeCN): OD = 0.5 at λ_{pump}. Samples were degassed by sparging with nitrogen. The sample was flowed (0.25 mLmin^{-1}) continuously through a quartz cuvette (b=1mm) during acquisition.

Pump Beam : λ = 422 nm (Alizarin) or 478 nm (Purpurin), beam diameter ≈ 300µm, pulsewidth ~110 fs, pulse energy at the sample = 2 µJ.

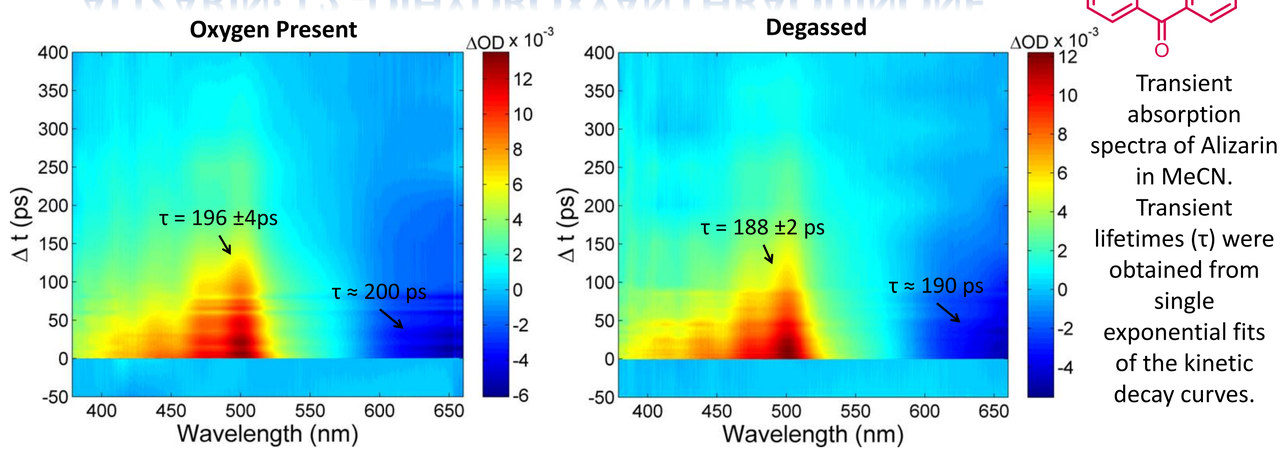
Probe Beam: Supercontinuum (~400-700nm), generated in a continuously rotating, 2mm thick CaF_2 plate. Beam diameter at sample ≈ 100 µm.

References

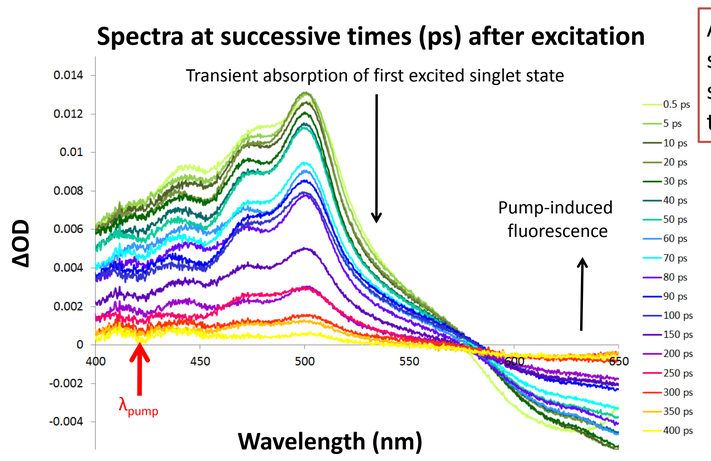
1. Casadio, F.; Leona, M.; Lombardi, J. R.; Van Duyne, R. *Acc. Chem. Res.* **2010**, 43, 782-791.
2. Saunders, D.; Kirby, J. *Nat. Gall. Tech. Bull.* **1994**, 15, 79-97.
3. Thompson, S.J., Rohde, C. A , Griffey, E, Simpson, M. C. Ultrafast Laser Studies of the Characteristics and Timescales of Photodegradation in Red Lake Dyes , *Lasers in the Conservation of Artworks.* (Proceedings of the International Conference LACONA IX held in London, United Kingdom 7-10 September **2011**). In press.
4. Clementi, C.; Nowik, W.; Romani, A.; Cibin, F.; Favaro, G. *Anal. Chim. Acta.* **2007**, 596, 46-54.

Analysis and Results

Alizarin: 1,2,-Dihydroxyanthraquinone

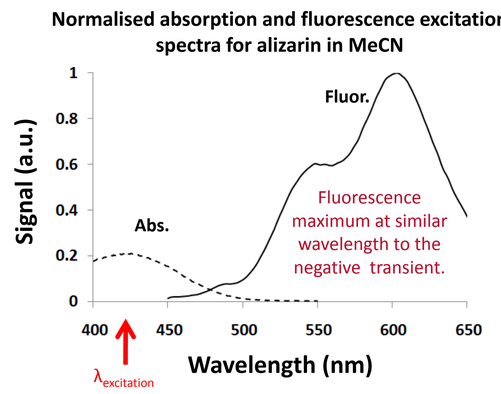


Transient absorption spectra of Alizarin in MeCN. Transient lifetimes (τ) were obtained from single exponential fits of the kinetic decay curves.



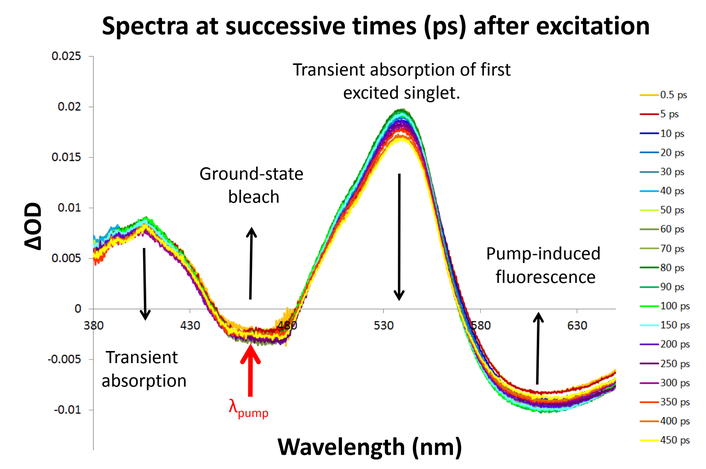
Temporal slices from the first spectrum above show the spectral evolution, indicated by the black arrows. As the absence of oxygen has only a very minimal effect, only one spectral overlay, for the oxygenated sample, is shown here. λ_{pump} indicates the TrA excitation wavelength.

Alizarin shows one structured transient absorption signal assigned to S_1 (τ ≈ 200 ps), and one negative signal assigned to pump-induced fluorescence from the same state (τ ≈ 200 ps).



Purpurin: 1,2,4-Trihydroxyanthraquinone

Transient absorption spectra of Purpurin in MeCN. Transient lifetimes (τ) were obtained from single exponential fits of the kinetic decay curves.

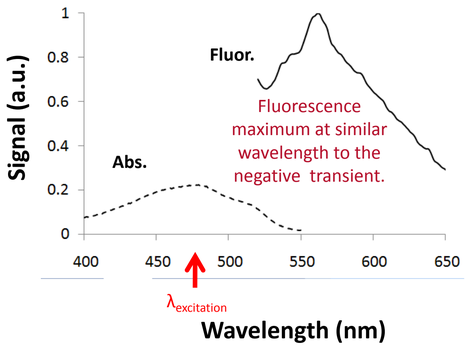


Temporal slices from the first spectrum above show the spectral evolution, indicated by the black arrows. As the absence of oxygen has only a very minimal effect, only one spectral overlay, for the oxygenated sample, is shown here. λ_{pump} indicates the TrA excitation wavelength.

Purpurin shows two transient absorption signals: one at ~ 410 nm (possibly due to a triplet state, at present unassigned) and another at ~540 nm, assigned to S_1 (τ ≈ 2 ns).

Two negative signals are present, one at ~460 nm, assigned to a ground-state bleach, and one at ~620 nm, assigned to pump-induced fluorescence from S_1 (τ ≈ 2 ns).

Purpurin has a much longer excited state lifetime than alizarin: it is therefore expected to be more vulnerable to photodegradation, which is entirely consistent with the reportedly superior photostability of alizarin.[4]



Conclusions & Future Work

These studies of alizarin and purpurin show a substantial difference in their responses to photoexcitation. The short excited state lifetime observed for alizarin compared to purpurin is consistent with the superior macroscopic photostability of alizarin reported in the literature.

The origin of the difference in excited state lifetimes for purpurin and alizarin is still under investigation. Though the effect of oxygen appears to be small, the impact of many other factors (such as excited-state intramolecular hydrogen bonding) on the stability and availability of decay pathways remains to be considered.

The Pazyryk Rug (section)