watching flowers through a silicon glass

multiscale simulation of the color optical properties of natural dyes

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati

Trieste — Italy

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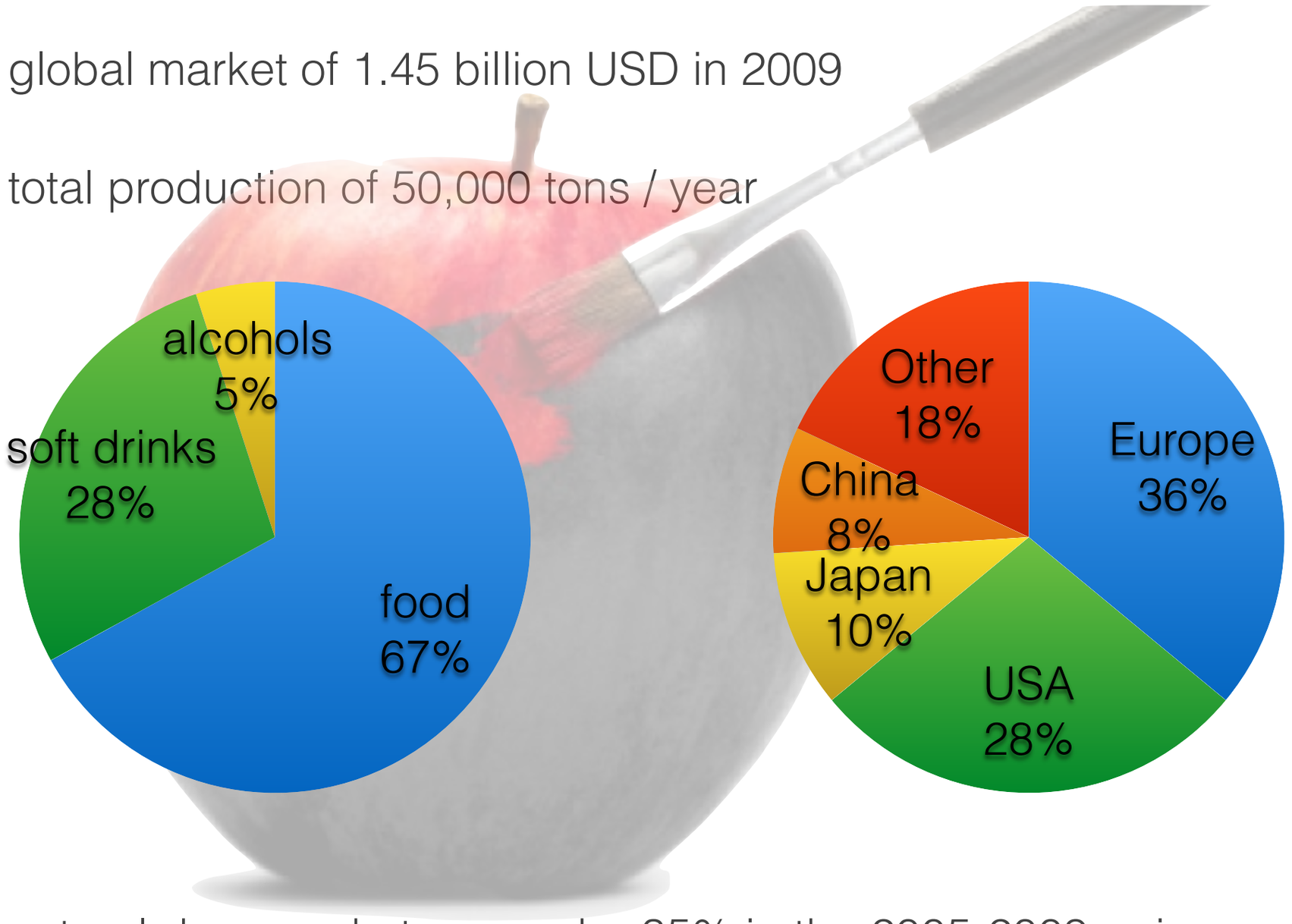
natural dyes in the food industry

natural dyes in the food industry

- global market of 1.45 billion USD in 2009
- total production of 50,000 tons / year



- natural dyes market grown by 35% in the 2005-2009 quinquennium

the food industry is subject to an increasing global pressure from customers and lawmakers who demand a shift towards ingredients and additives that are perceived as *more natural* and, “therefore”, *healthier*

the Southampton six

In 2007 Research funded by the UK FSA was published, suggesting that the consumption of certain mixes of artificial food colours and preservatives could be linked to attention deficit and increased hyperactivity in some children.

Box A: <u>The Seven Southampton Additives</u>

Colours:

- **Tartrazine (E102)**
- **Quinoline yellow (E104)**
- **Sunset yellow (E110)**
- **Carmoisine (E122)**
- **Ponceau 4R (E124)**
- **Allura red (E129)**

Preservative:

- **Sodium benzoate (E211)**

Since 2010 an EU-wide compulsory warning must be put on any food and drink product that contains any of these six colours:

“May have an adverse effect on activity and attention in children”

natural dyes: the requirements

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- tunable

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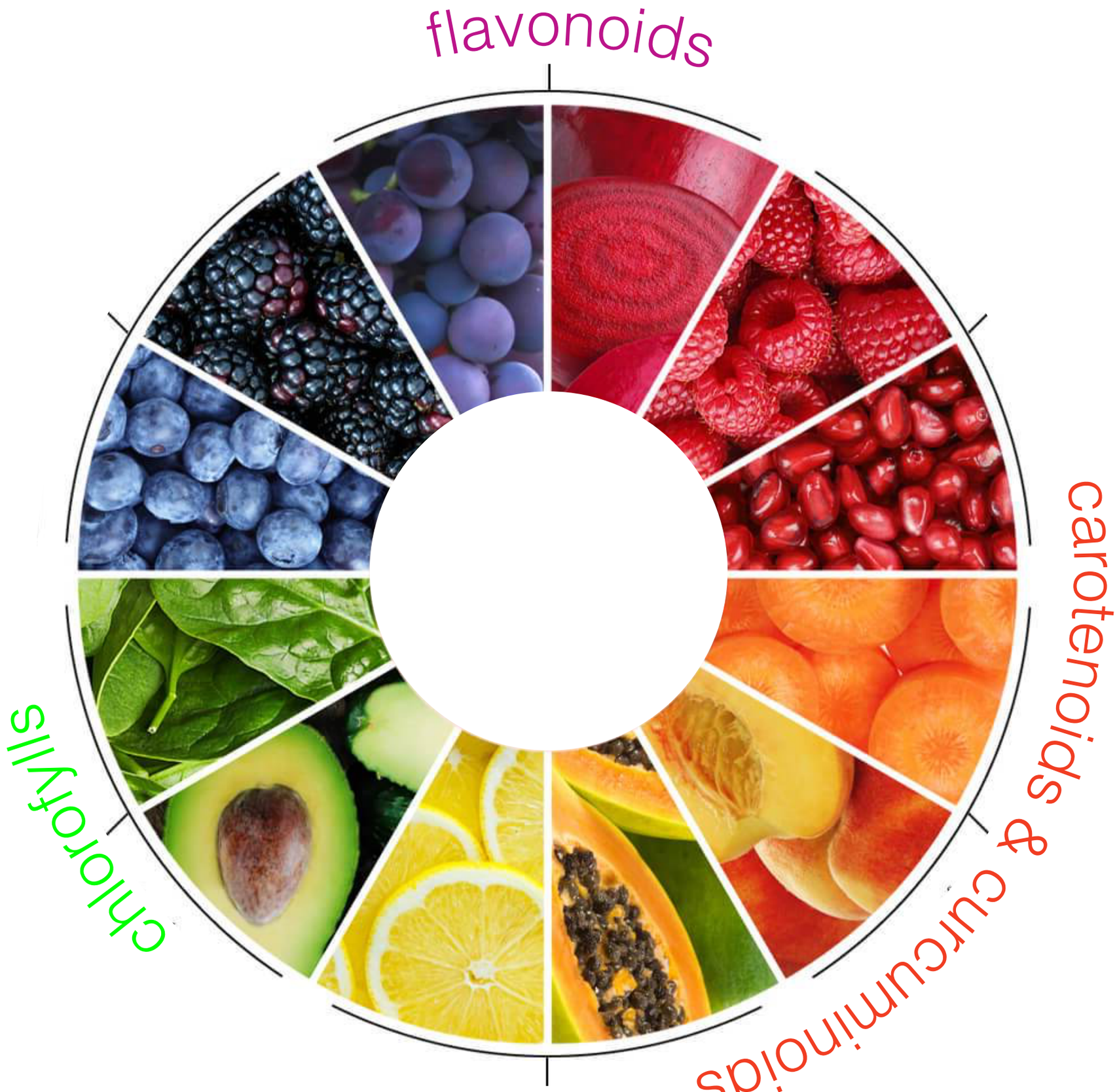
- tunable
- stable

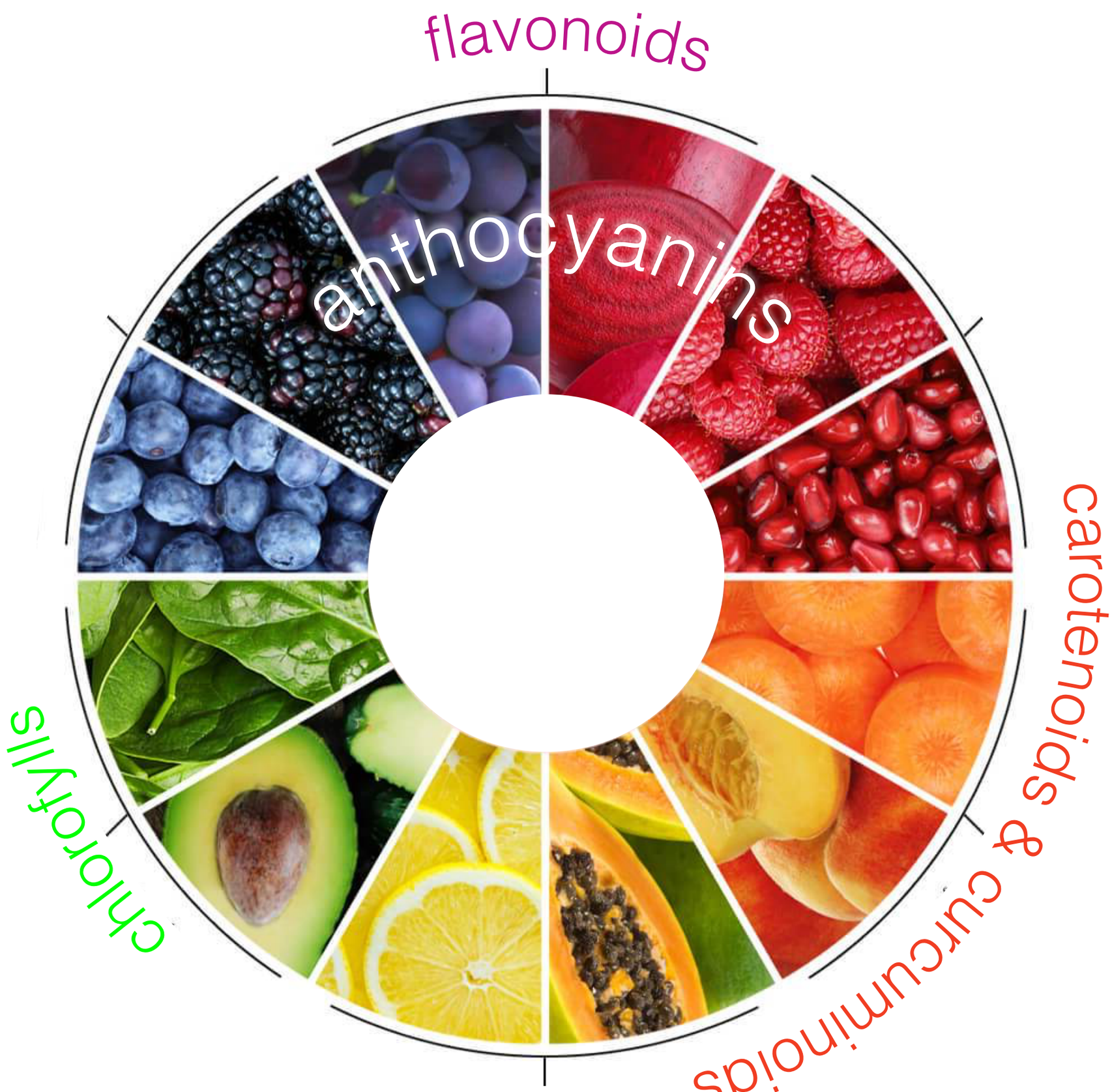
natural dyes: the requirements

- tunable
- stable
- safe

natural dyes: the requirements

- tunable
- stable
- safe
- inexpensive


flavonoids
carotenoids & curcuminoids
chlorophylls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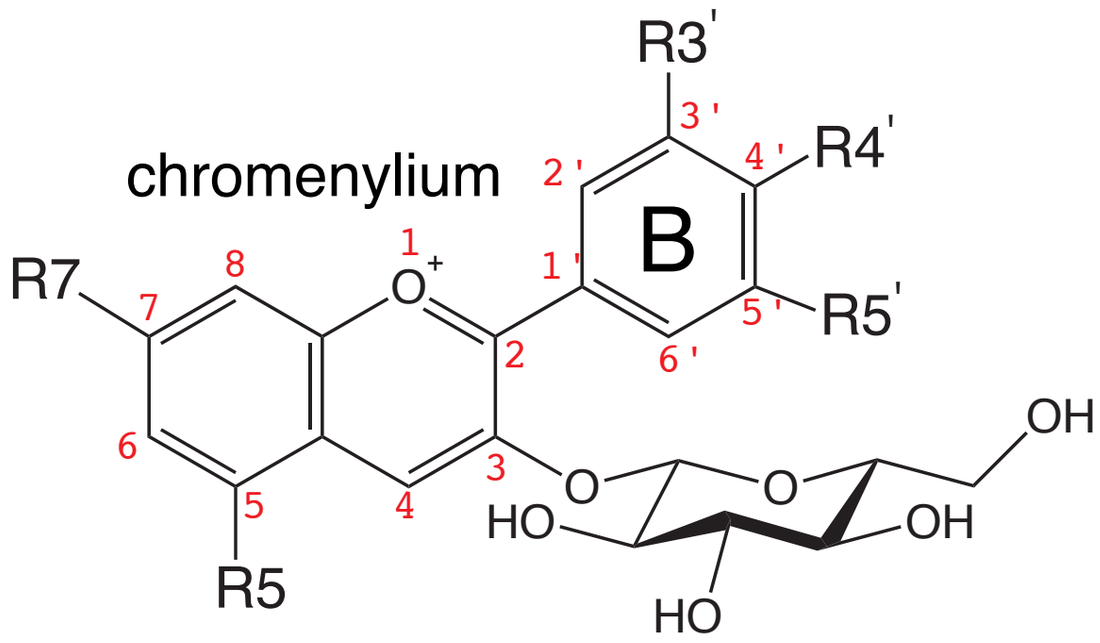
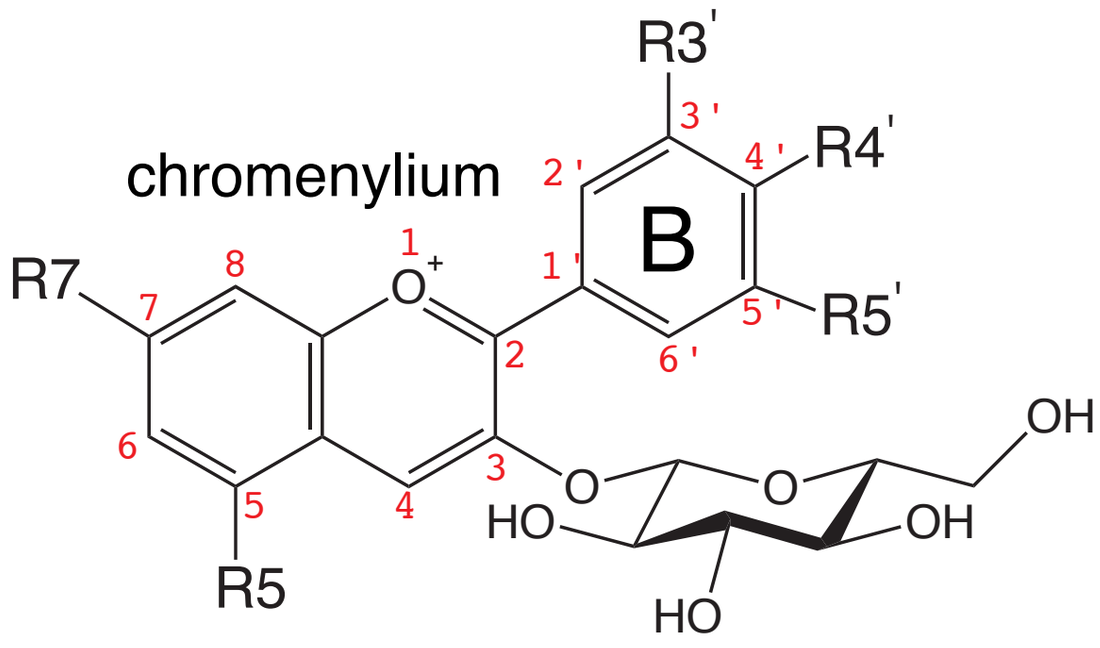
anthocyanins

MA PER SEGUIR VIRTUTE E CANOSCENZA

anthocyanins

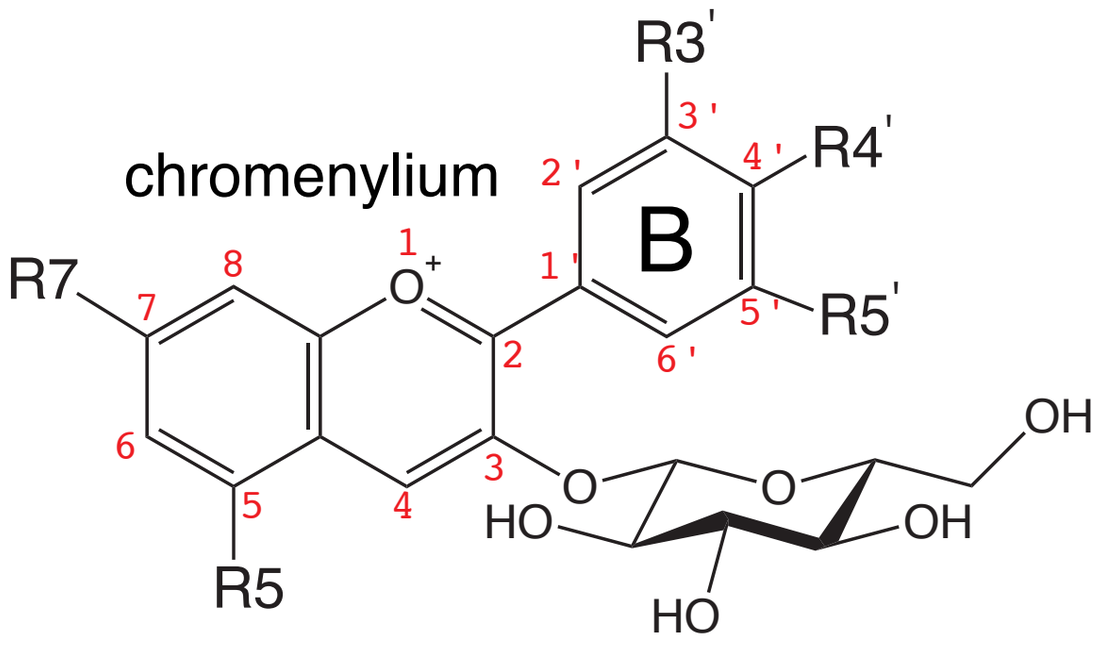


anthocyanins



anthocyanin	R3’	R4’	R5’	R7
cyanin	–OH	–OH	–H	–OH

anthocyanins



anthocyanin	R3’	R4’	R5’	R7
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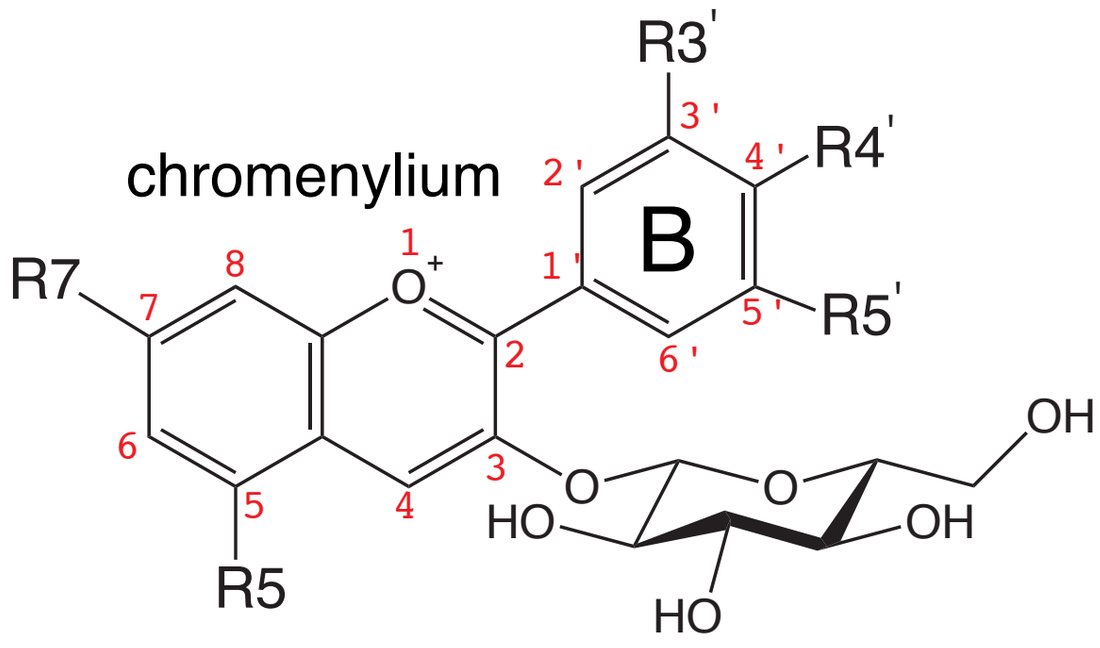
peonin	$–OCH_3$	–OH	–H	–OH

anthocyanins



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rosinin	–OH	–OH	–H	$–OCH_3$

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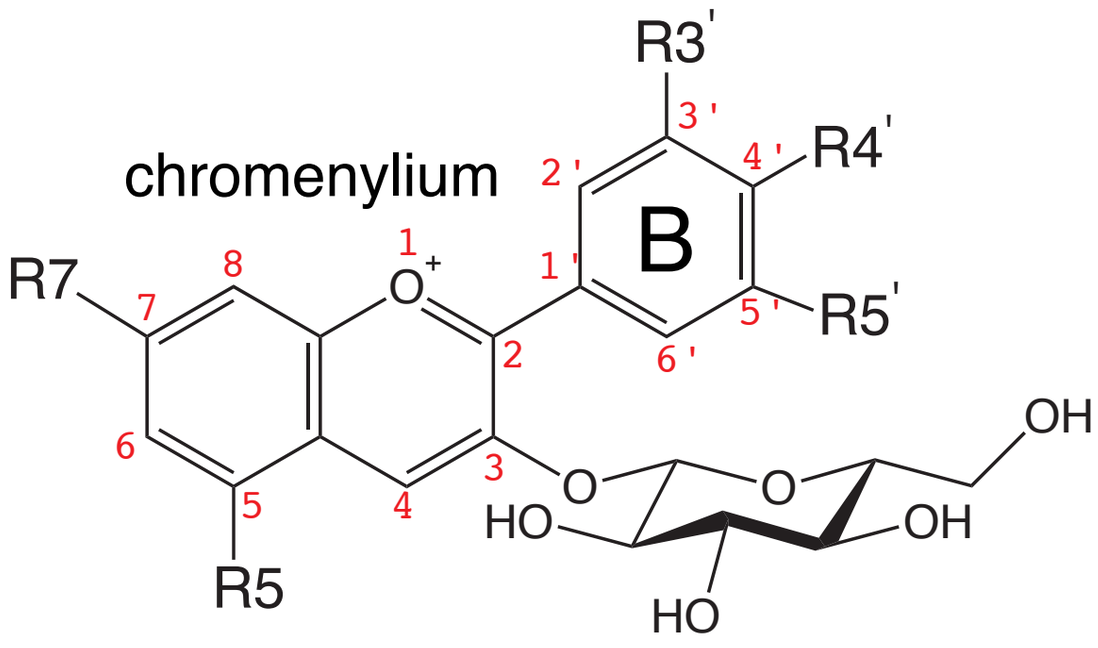

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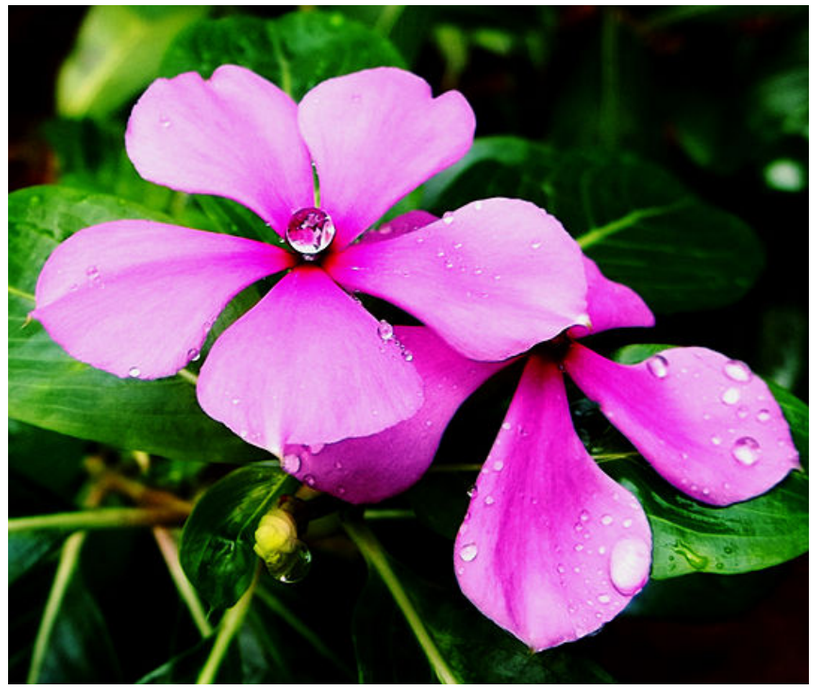
malvin	$–OCH_3$	–OH	$–OCH_3$	–OH



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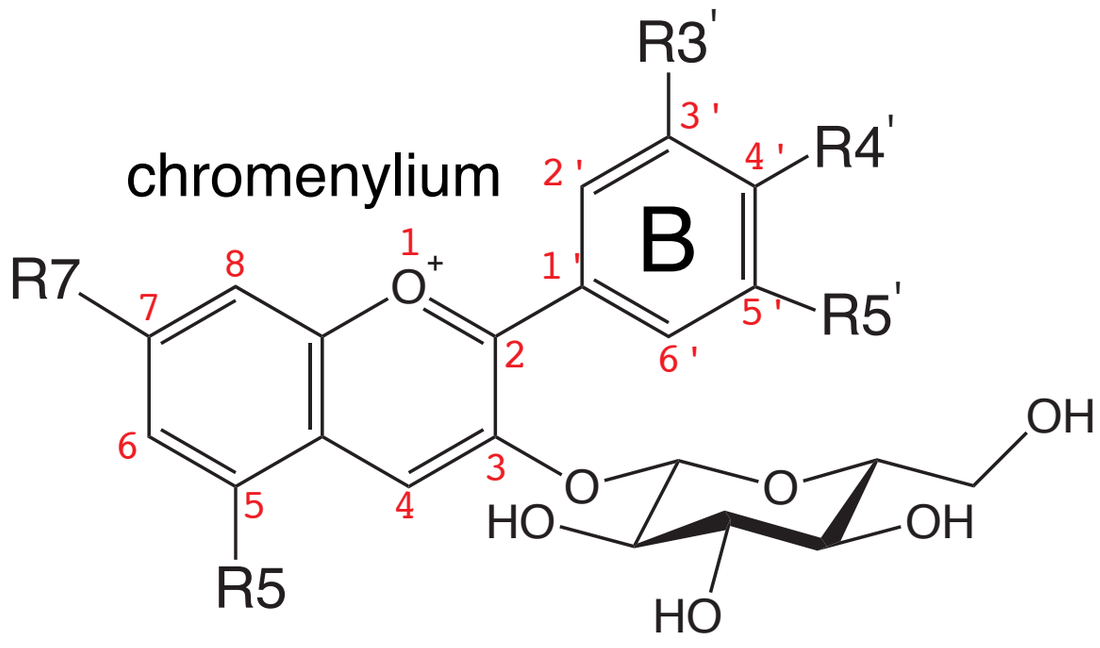

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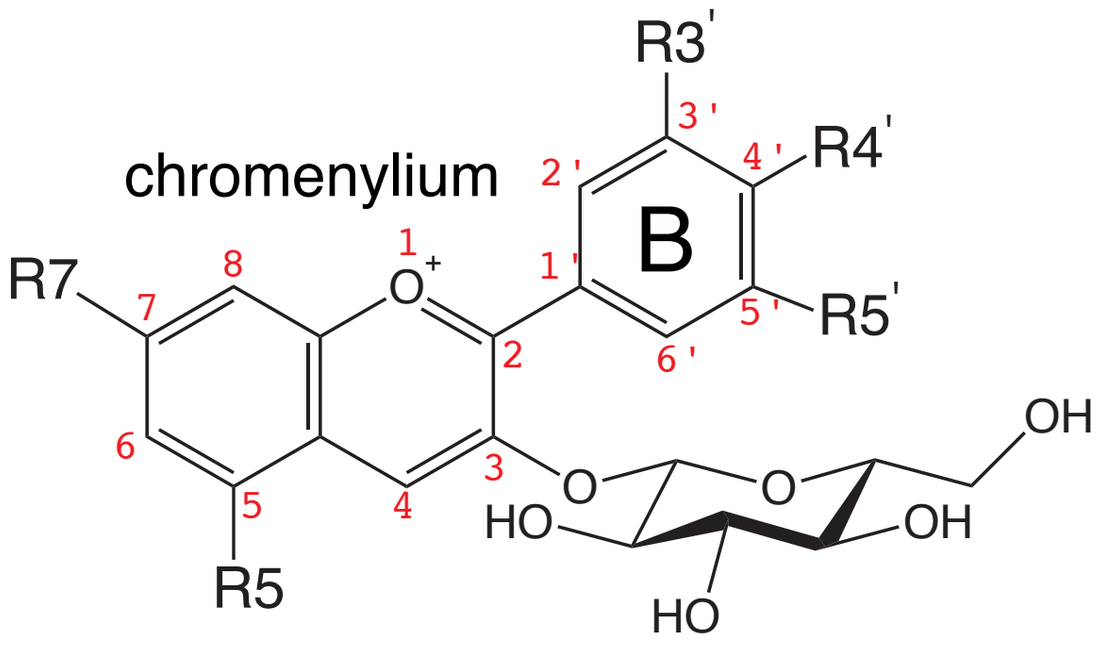
pelargonin	–H	–OH	–OH	–OH

anthocyanins



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rosinin	–OH	–OH	–H	$–OCH_3$
malvin	$–OCH_3$	–OH	$–OCH_3$	–OH
pelargonin	–H	–OH	–OH	–OH
delphinin	–OH	–OH	$–OCH_3$	–OH

very little is known of the molecular mechanisms that determine the chromatic properties and the stability of anthocyanins and the relation between structure and color

what color is all about

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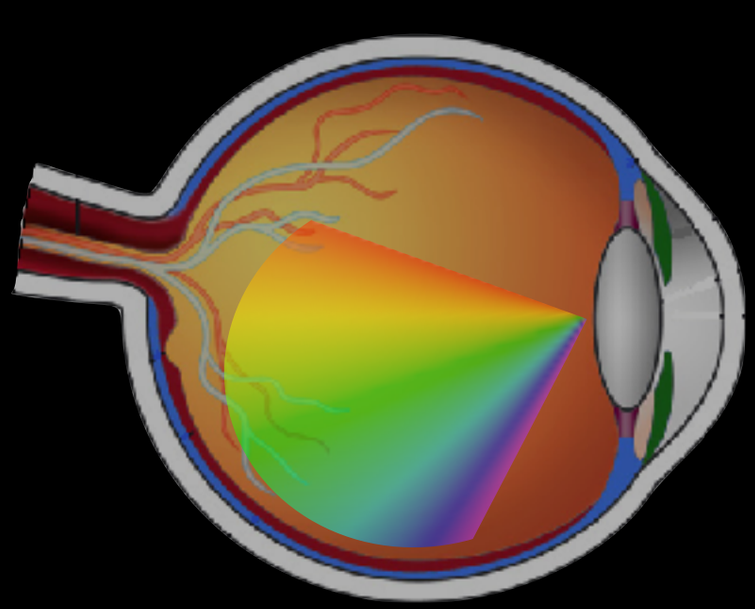

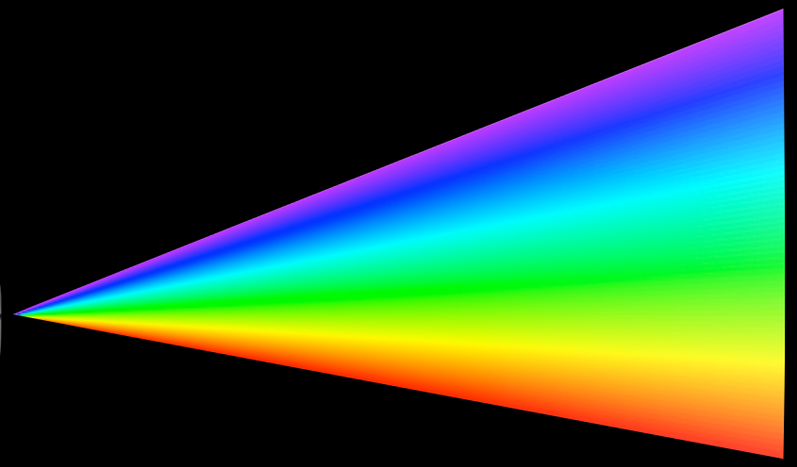

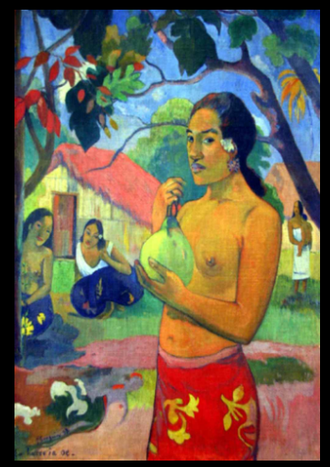

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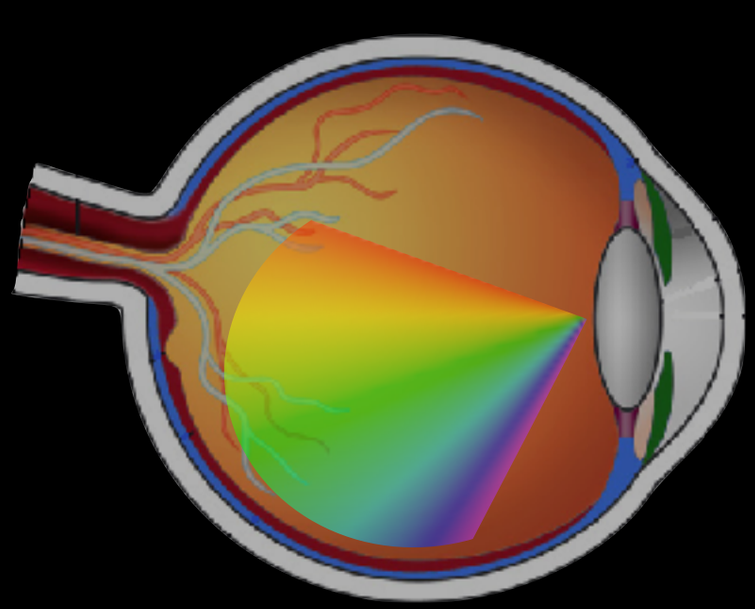

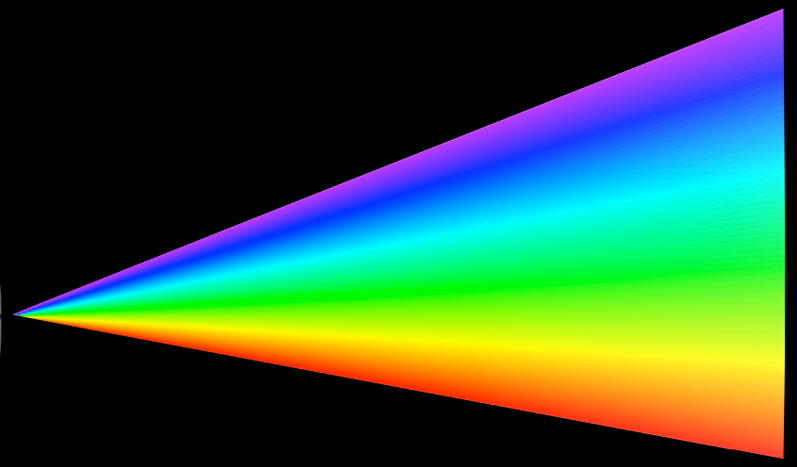

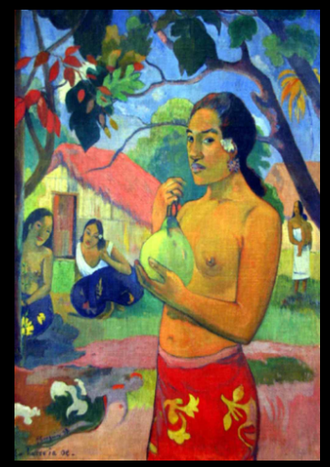

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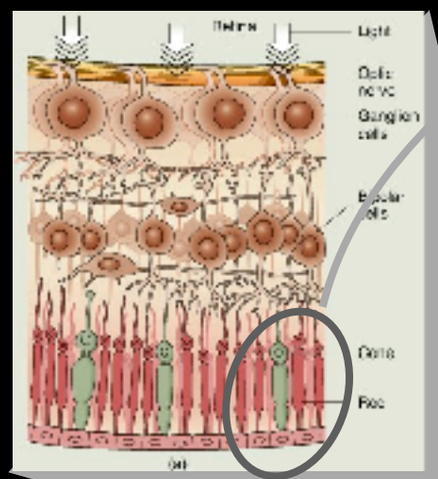

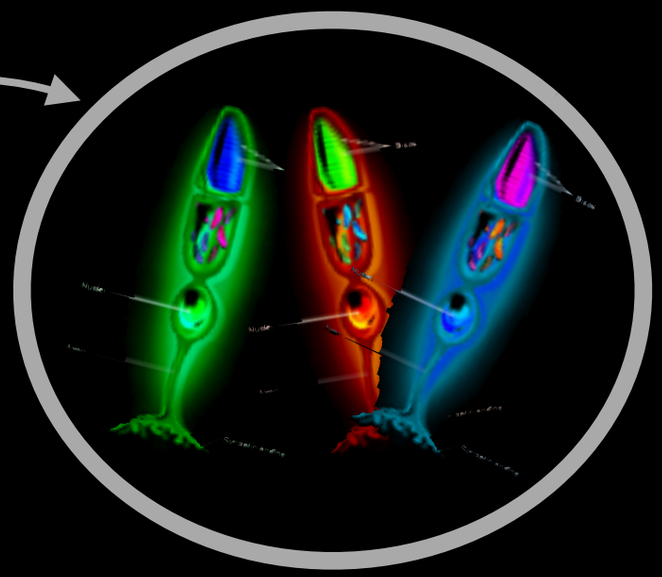

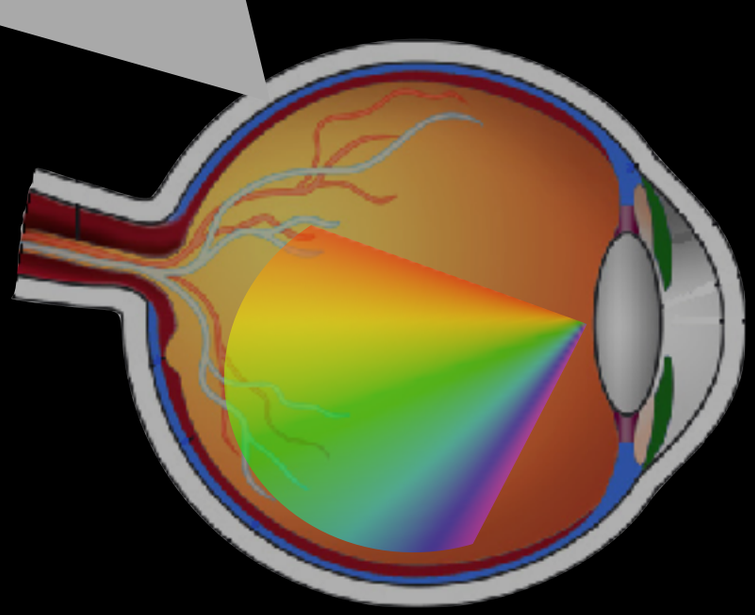

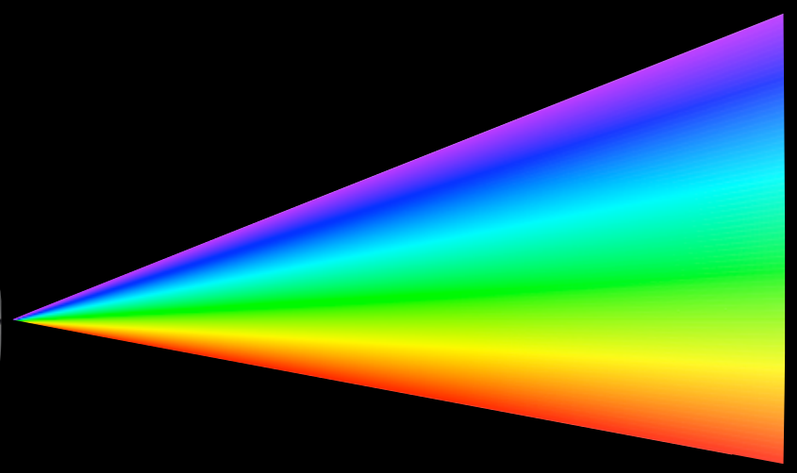

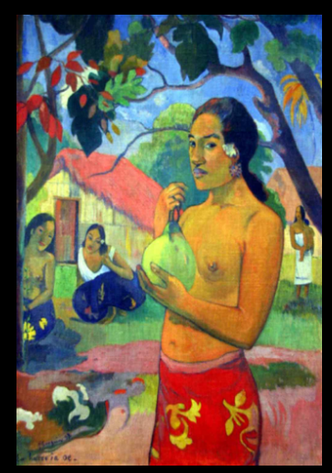

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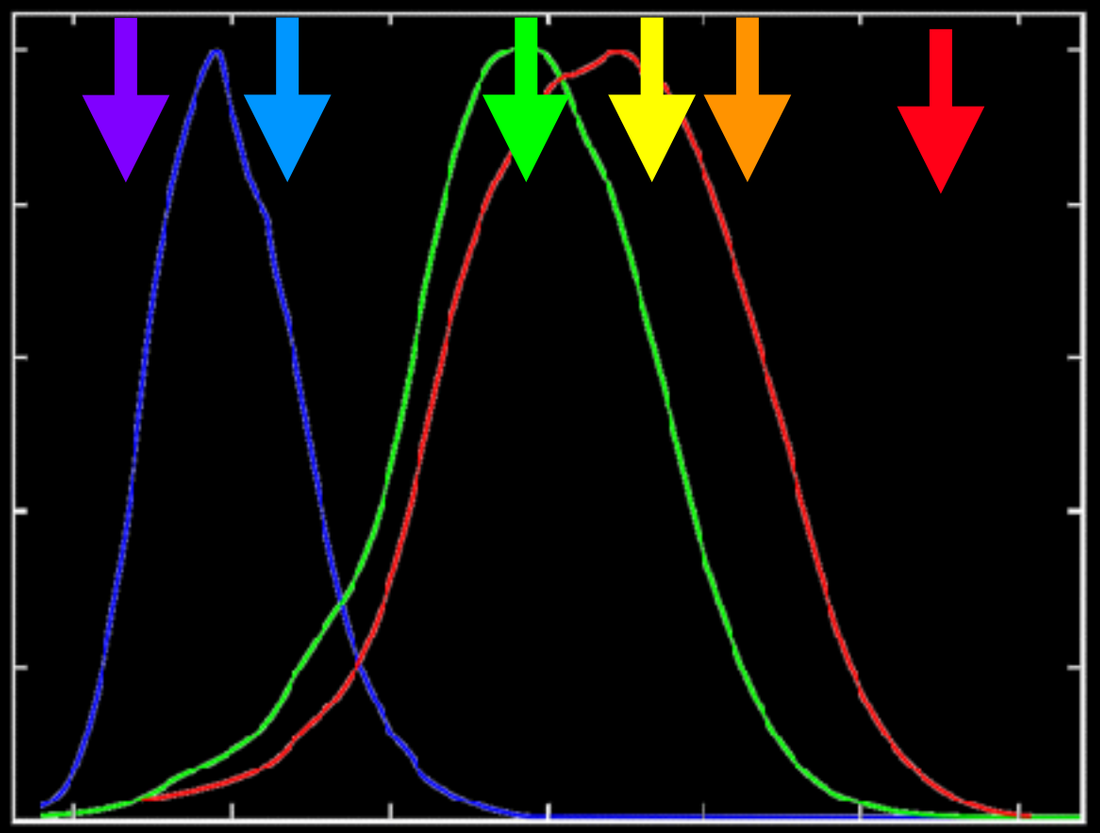
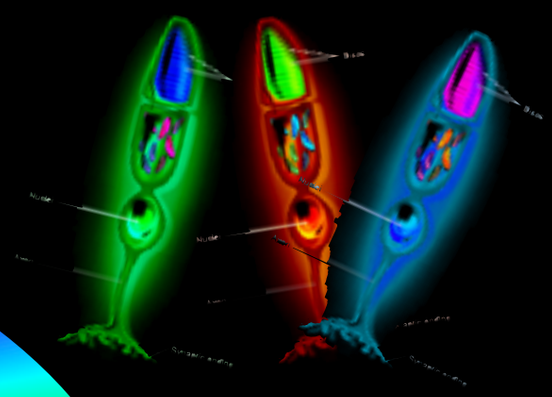
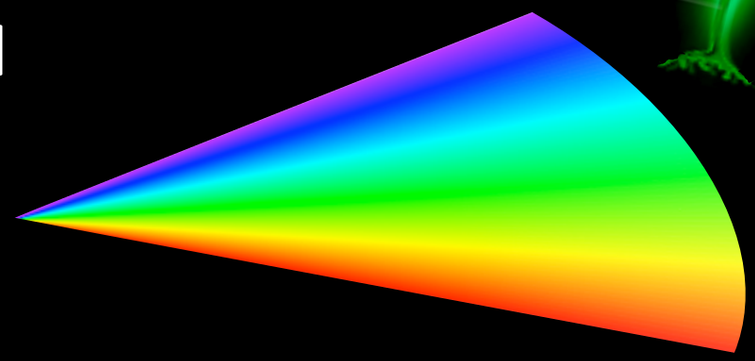


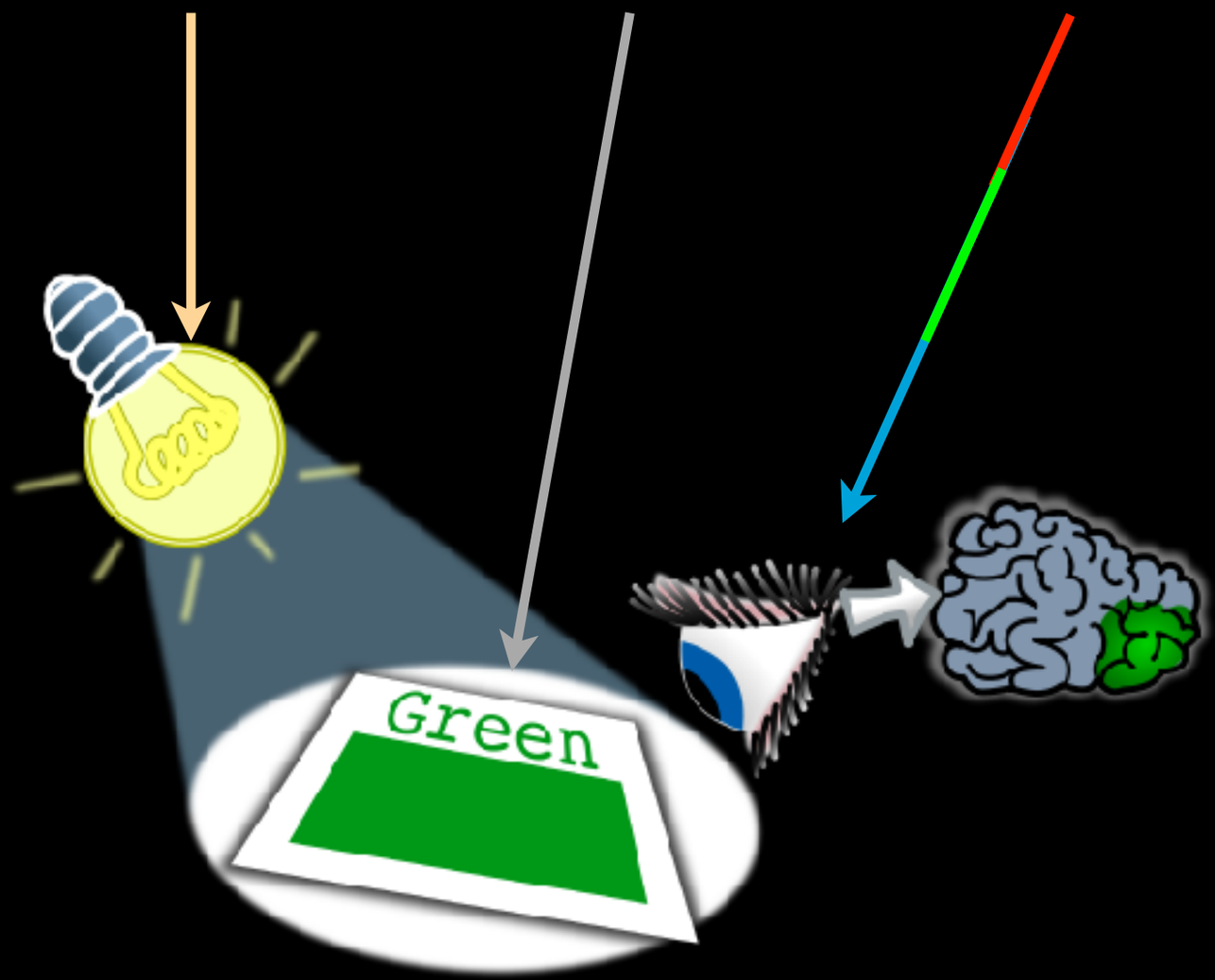


anycolor(λ) = r(λ) + g(λ) + b(λ)



what color is all about

stimulus =
illuminant × transmission × sensitivity



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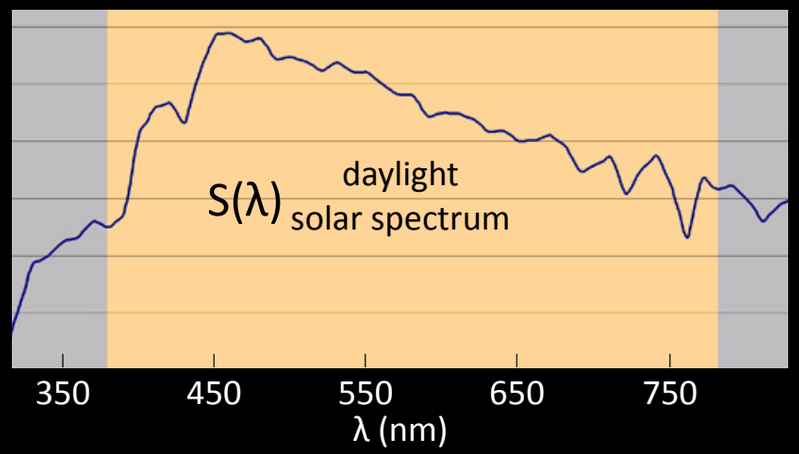
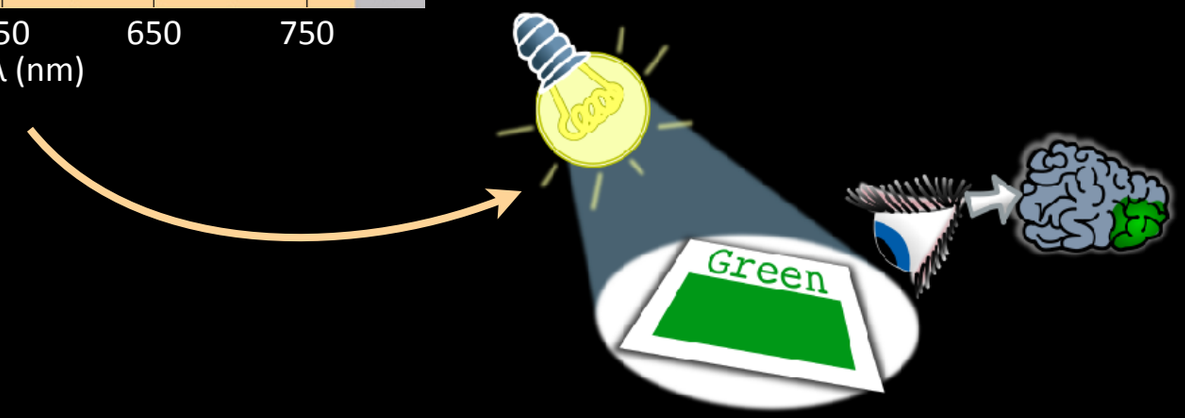
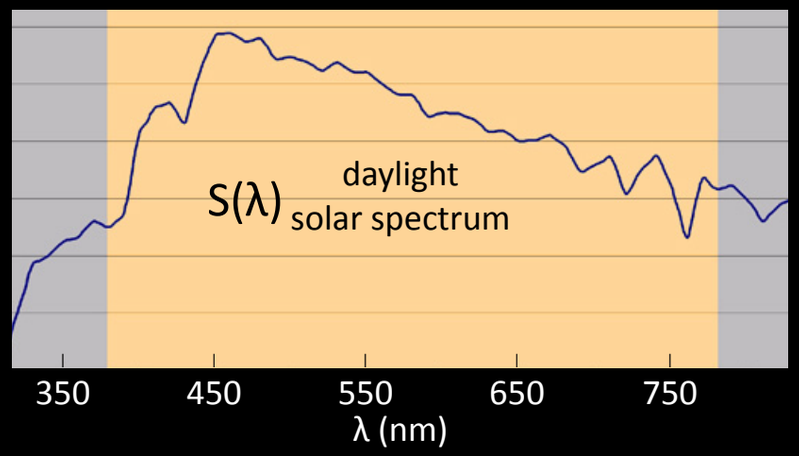


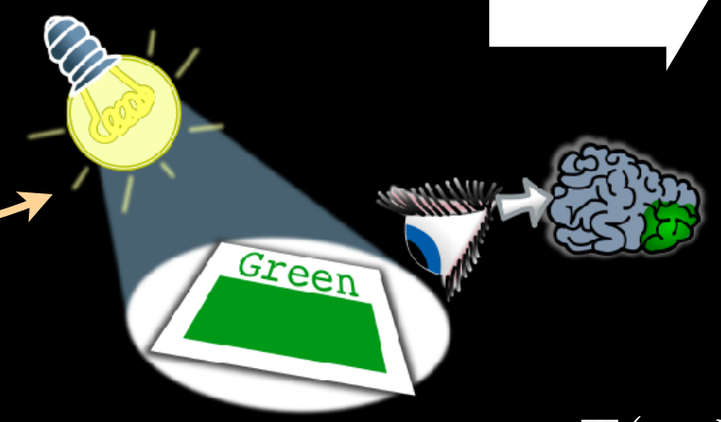


stimulus =
illuminant × transmission × sensitivity

$S(\lambda)$

what color is all about

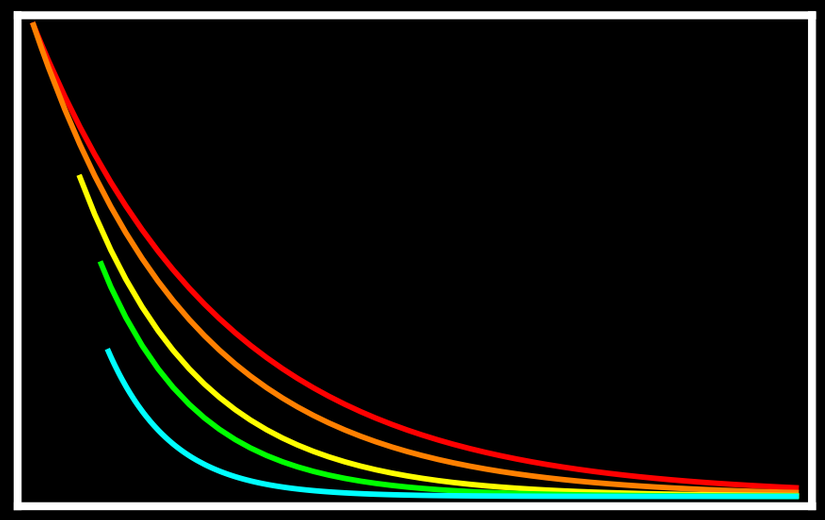




light

absorbing medium

$\mathsf{T}(x, \lambda)$



x

stimulus =
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$\mathsf{S}(\lambda)$

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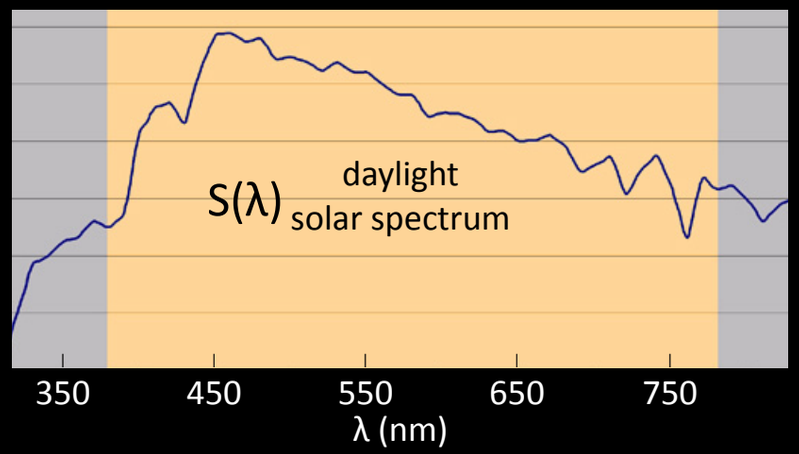

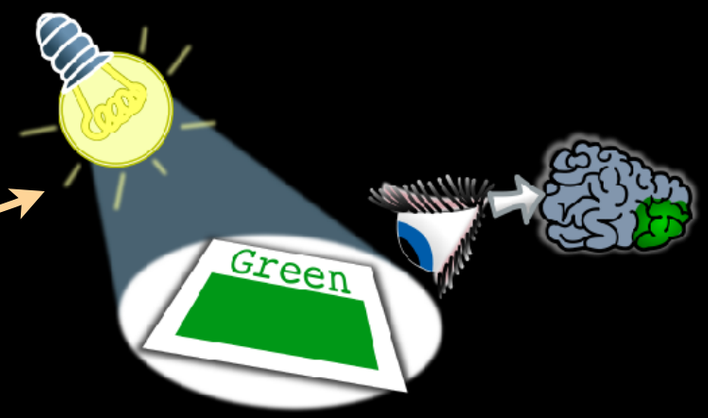

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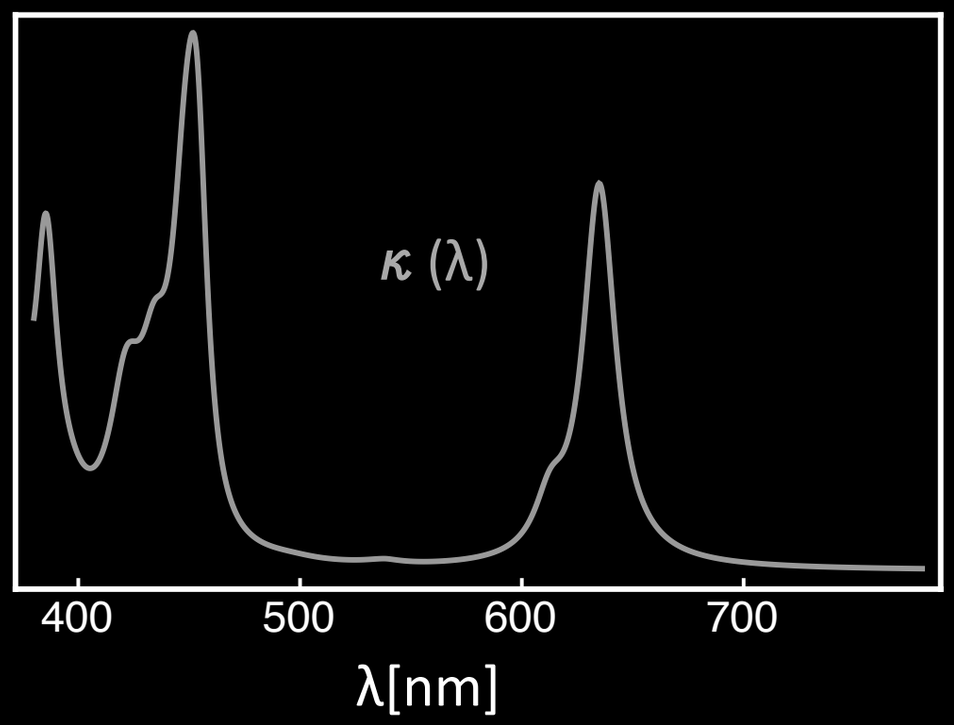
$$S(\lambda) \times e^{-\kappa(\lambda)x}$$



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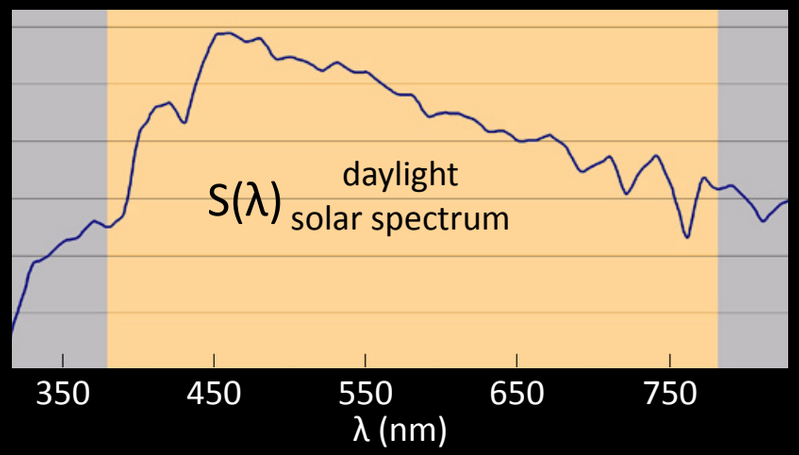

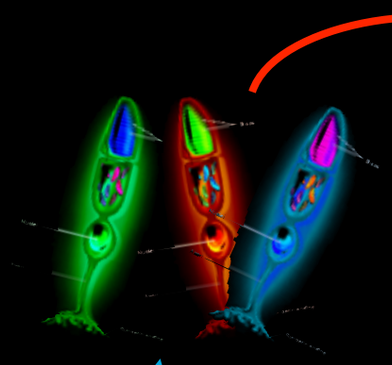

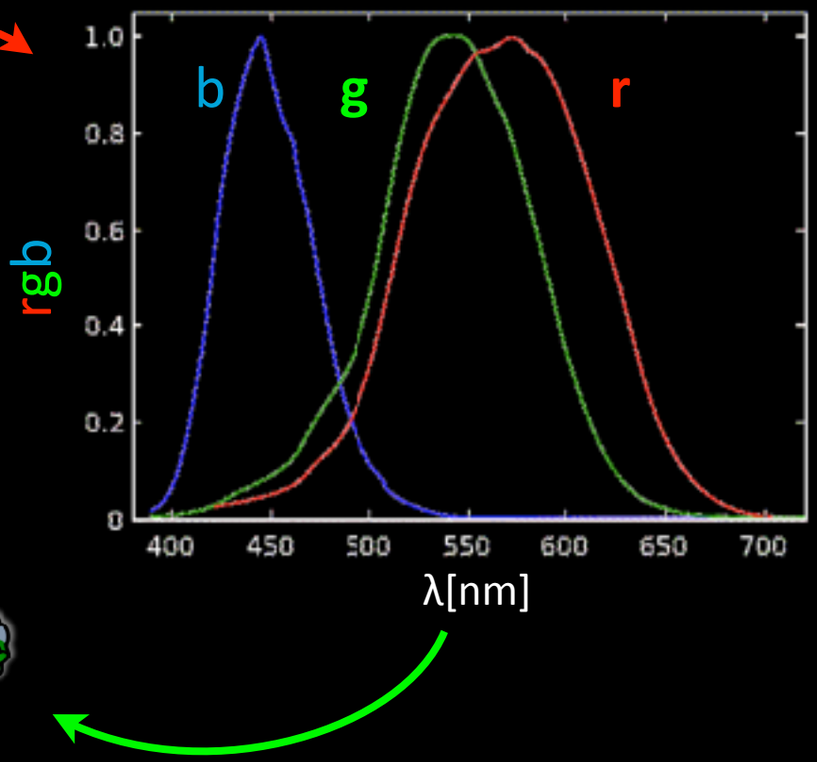

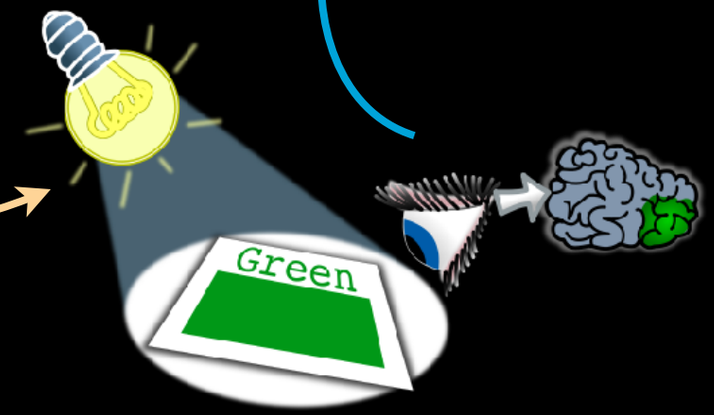

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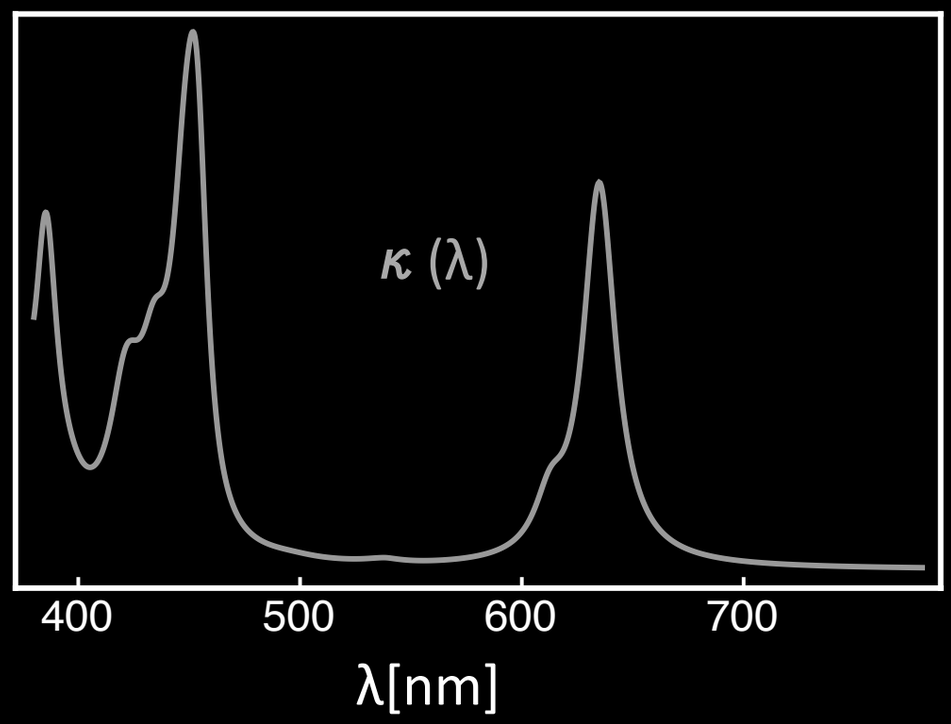
$$S(\lambda) \times e^{-\kappa(\lambda)x} \times rgb(\lambda)$$



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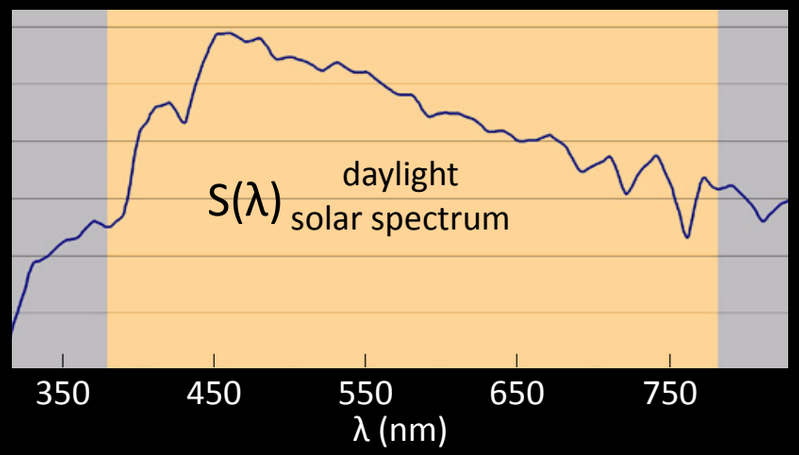

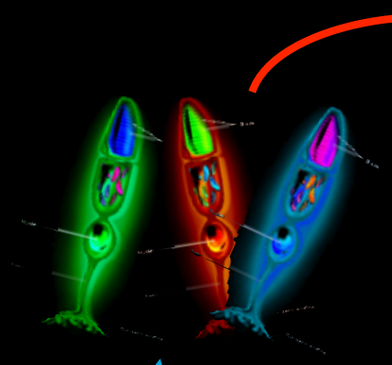

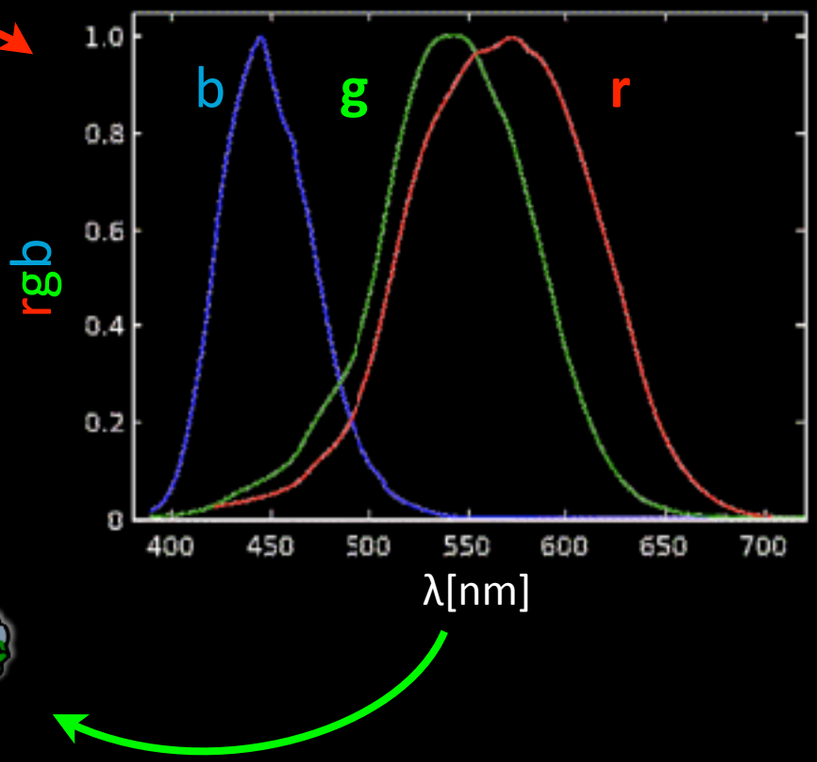

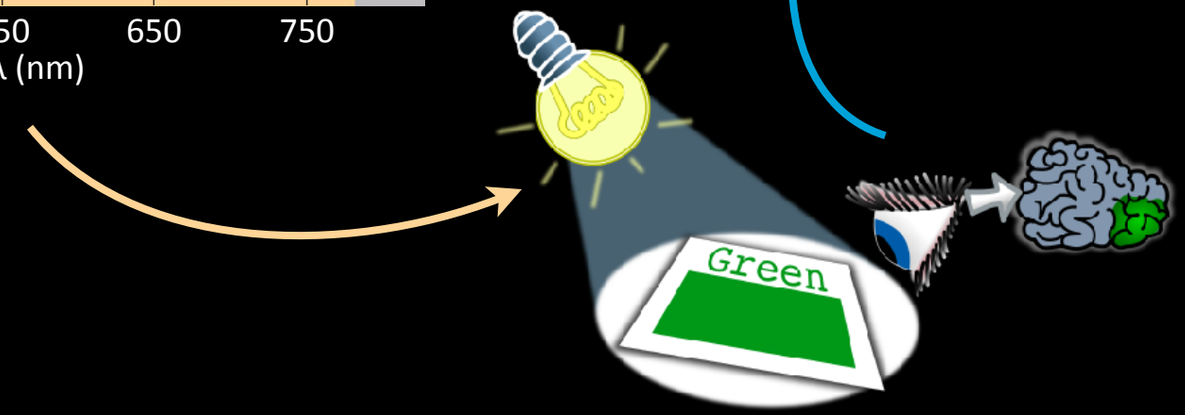

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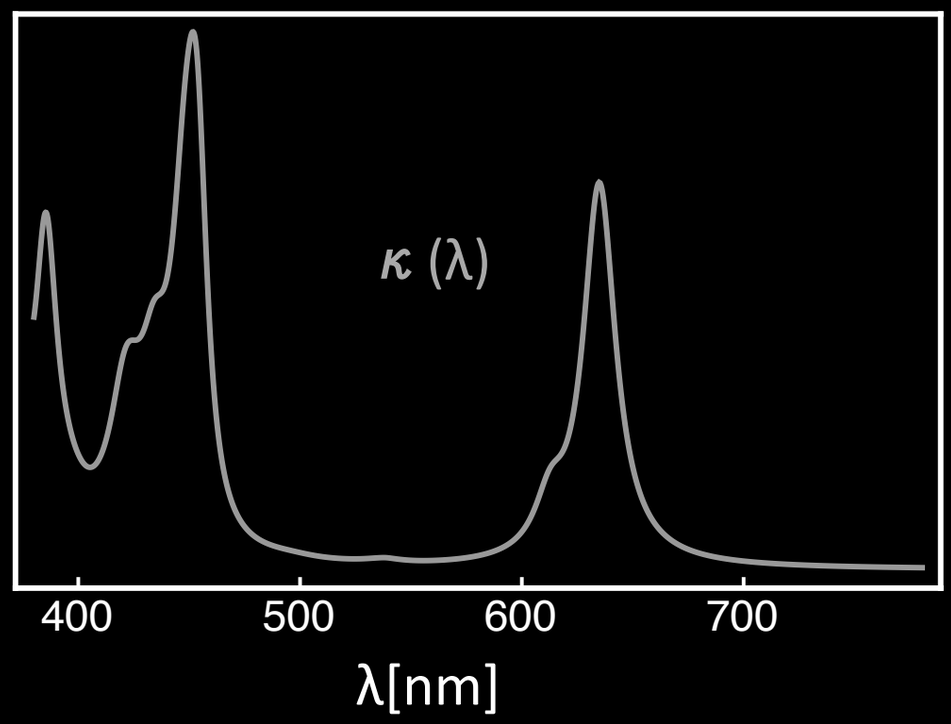
$$\mathrm{RGB}(x) = \int \mathrm{S}(\lambda)\mathrm{e}^{-\kappa(\lambda)x}\mathrm{rgb}(\lambda)d\lambda$$



how to predict the color optical properties of materials?

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

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optical spectra from TDDF(p)T

$$n(\mathbf{r},t) = \sum_v |\phi_v(\mathbf{r},t)|^2$$

$$i\frac{\partial \phi_v(\mathbf{r},t)}{\partial t} = \big(-\Delta + v_{KS}(\mathbf{r},t)\big)\phi_v(\mathbf{r},t)$$

$$v_{KS}(\mathbf{r},t) = v^{\circ}(\mathbf{r}) + E(t)\,x + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n](\mathbf{r},t)$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

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$$\rho(t) = \sum_v |\phi_v(t)\rangle\langle\phi_v(t)|$$

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$$i\dot{\rho}(t) = \big[H_{KS}(t), \rho(t)\big]$$

optical spectra from TDDF(p)T

$$i\dot{\rho}(t) = \left[H_{KS}(t), \rho(t)\right]$$

$$\rho(t) = \rho^{\circ} + \rho'(t)$$
$$H_{KS}(t) = H^{\circ} + E(t)x + V'_{HXC}(t)$$

$$i\ \dot{\rho}' = [H^{\circ},\rho'] + [V'_{HXC}, \rho^{\circ}] + E[x, \rho^{\circ}] + \mathcal{O}\left(E^2\right)$$

optical spectra from TDDF(p)T

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$$i\ \dot{\rho}'(t) = \mathcal{L}\ \rho'(t) + E(t)[x, \rho^{\circ}]$$

optical spectra from TDDF(p)T

$$i\dot{\rho}(t) = \left[H_{KS}(t), \rho(t)\right]$$

$$\rho(t) = \rho^{\circ} + \rho'(t)$$
$$H_{KS}(t) = H^{\circ} + E(t)x + V'_{HXC}(t)$$

$$i\ \dot{\rho}' = [H^{\circ},\rho'] + [V'_{HXC}(\rho'), \rho^{\circ}] + E[x, \rho^{\circ}]$$

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = \tilde{E}(\omega)[x, \rho^{\circ}]$$

optical spectra from TDDF(p)T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = \tilde{E}(\omega)[x, \rho^\circ]$$

$$\alpha(\omega) \equiv \left(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [x, \rho^\circ]\right)$$

TDDF(p)T: Lanczos' recursion method

optical spectra from TDDF(p)T

$$(\omega - \mathcal{L})\tilde{\rho}'(\omega) = \cancel{\tilde{E}(\omega)[x, \rho^\circ]}$$

$$\alpha(\omega) \equiv \left(\mathbf{d}, (\omega - \mathcal{L})^{-1} \cdot [x, \rho^\circ]\right)$$

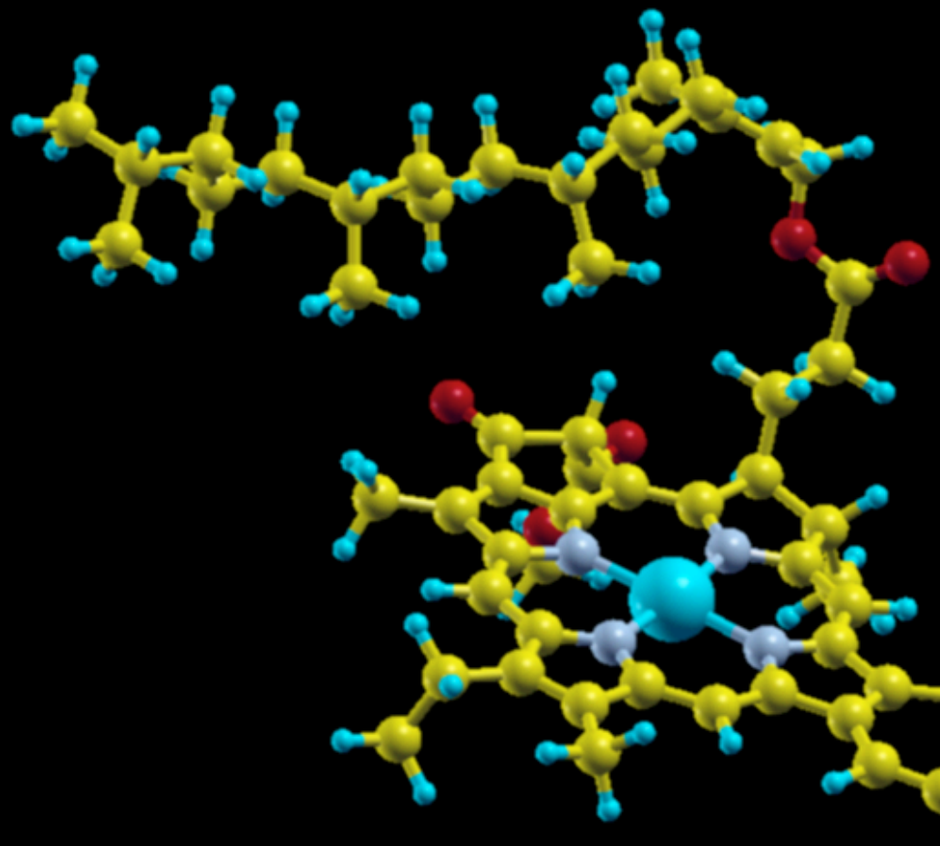
TDDF(p)T: Lanczos' recursion method

$$\mathcal{L}\ \tilde{\rho}' = \omega \tilde{\rho}'$$

Casida's equations: iterative diagonalization of large matrices (DIIS or Davidson)

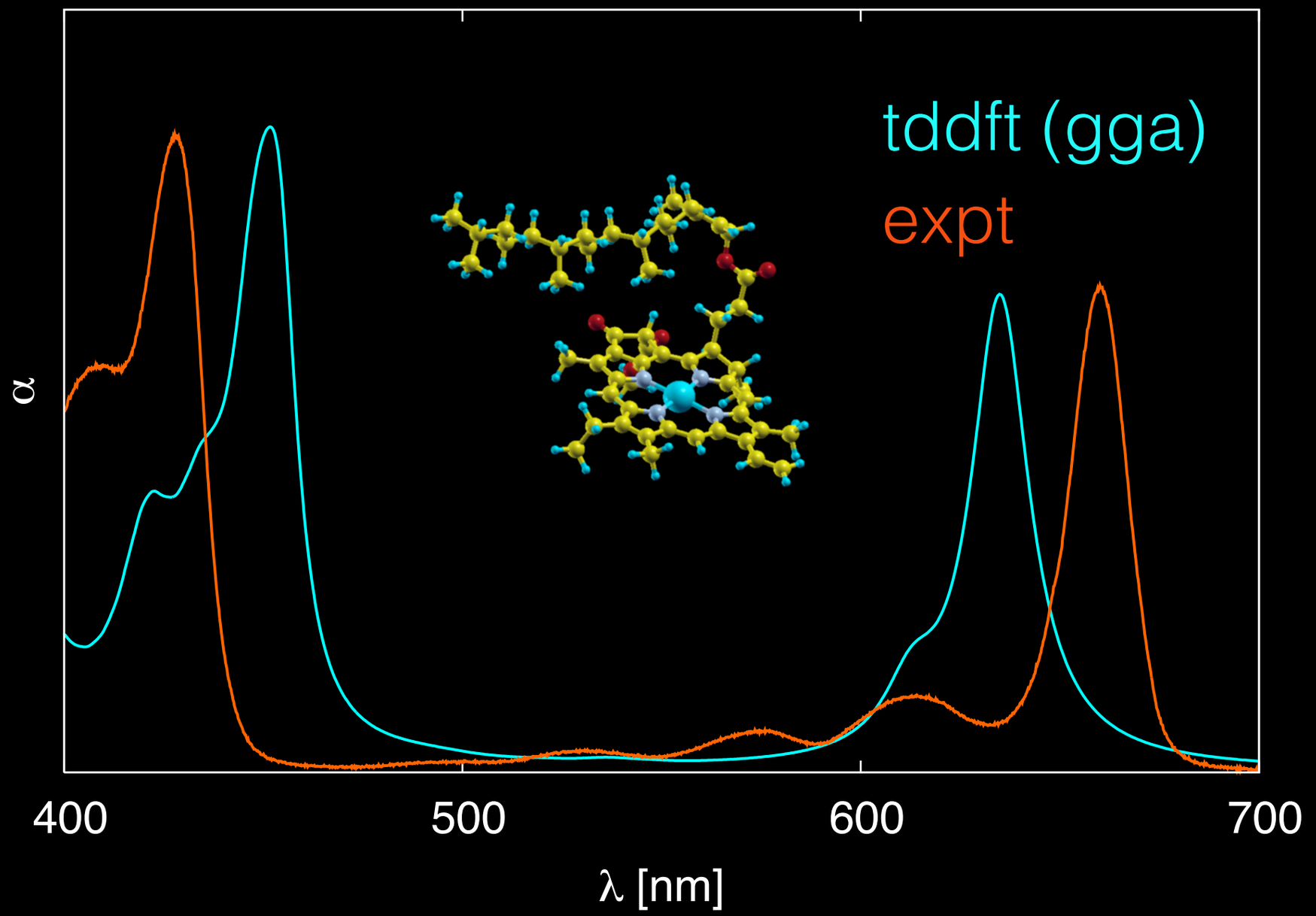
D. Rocca et al. JCP **128**, 154105 (2008)
X. Ge et al. Comp. Phys. Commun. **185**, 2080 (2014)

chlorophyll a

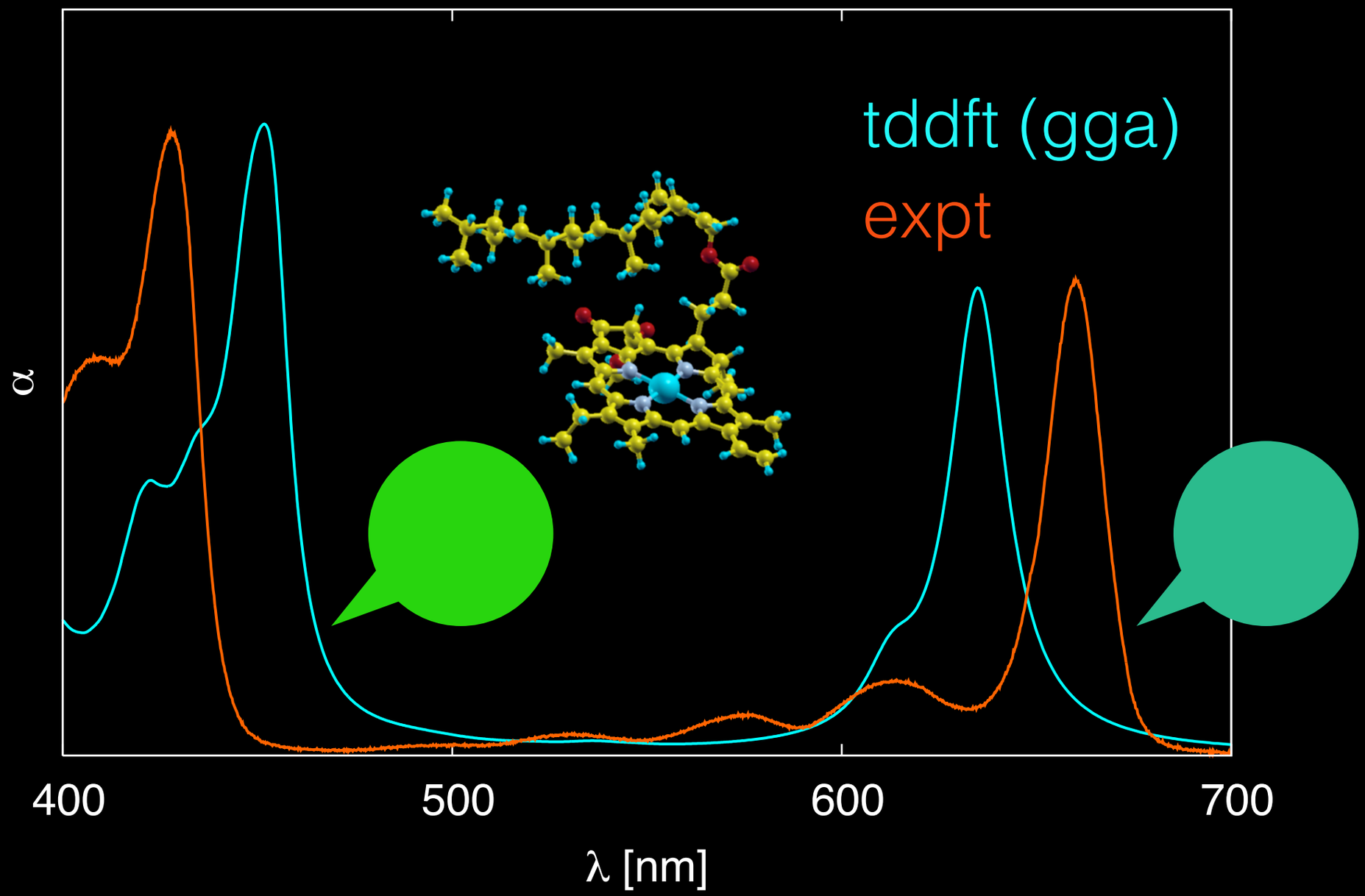


$C_{55}H_{72}MgN_4O$

chlorophyll a

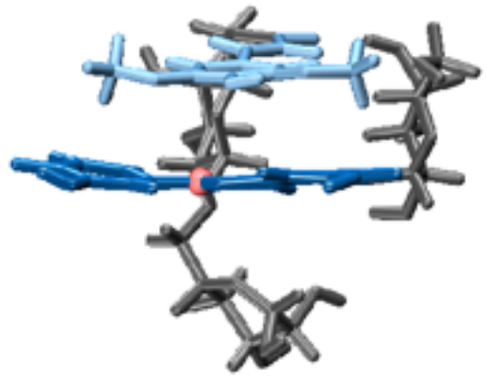


chlorophyll a



from chemistry to color

chemical composition → molecular structure



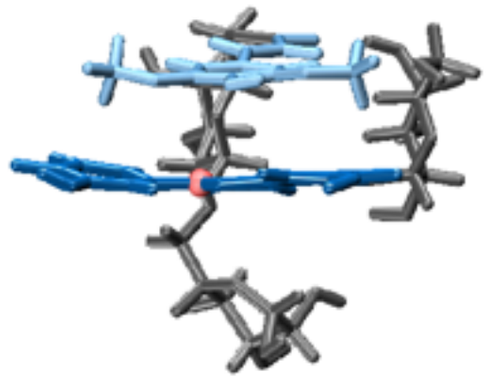
from chemistry to color

chemical composition

+

environmental conditions

molecular structure



from chemistry to color

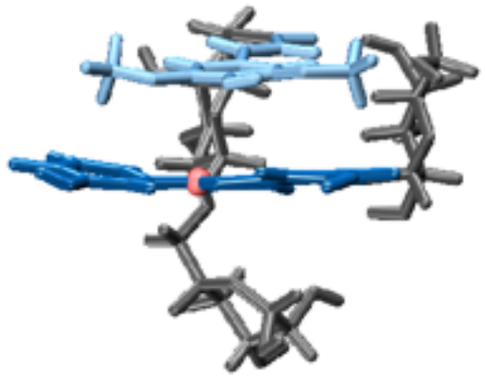
chemical composition

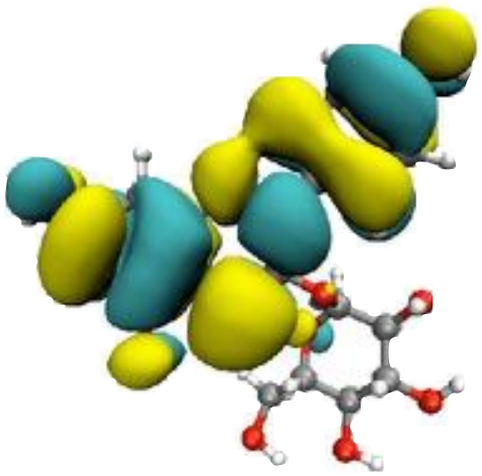
+

environmental conditions

molecular structure

electronic structure





from chemistry to color

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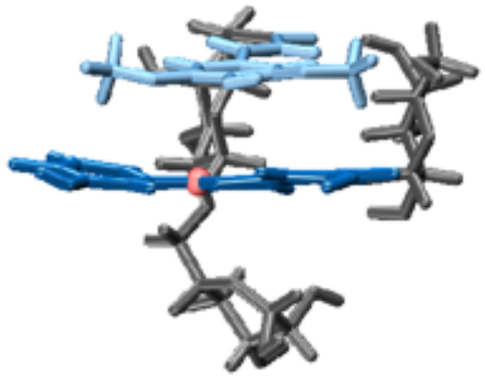
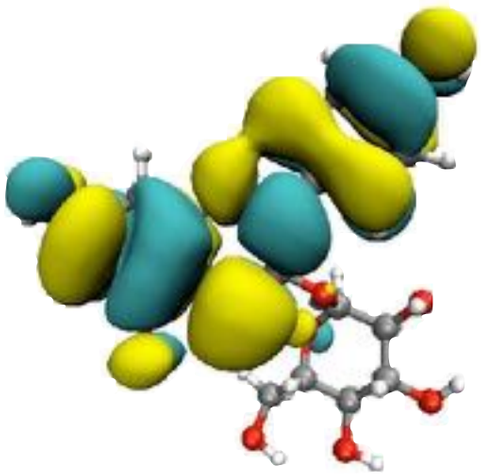
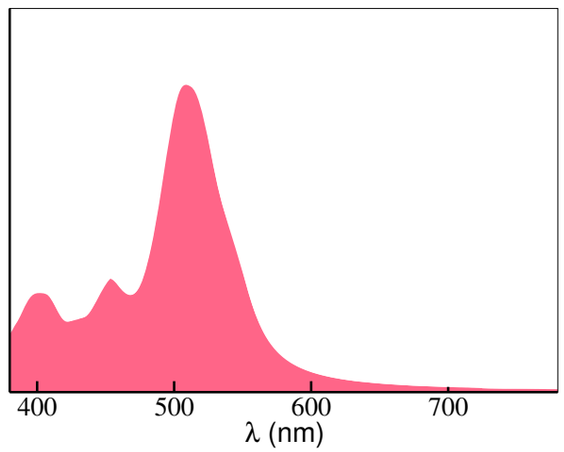
molecular structure

electronic structure

absorption spectrum







from chemistry to color

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=

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electronic structure

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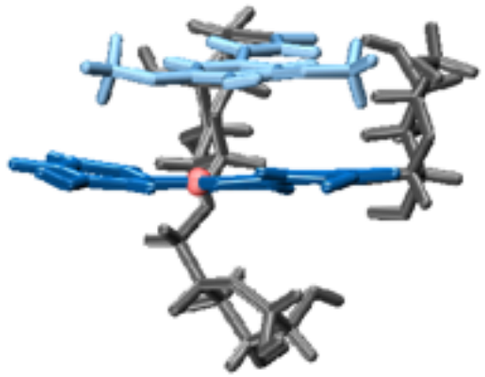
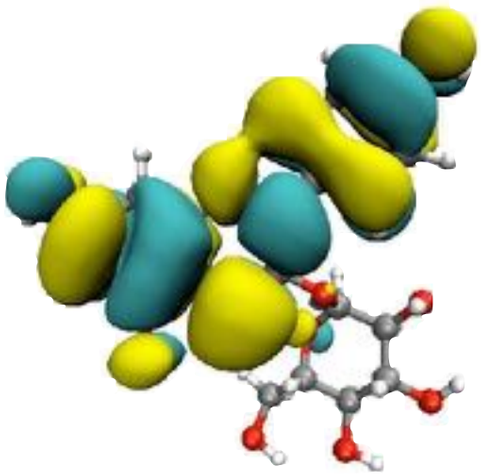
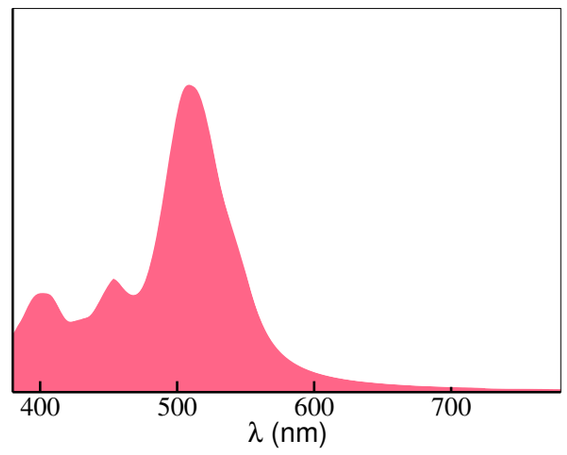
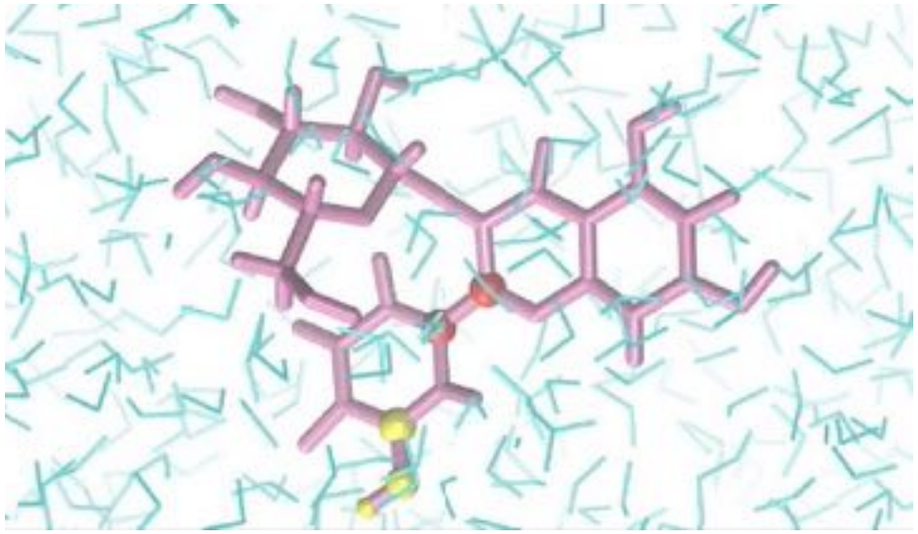
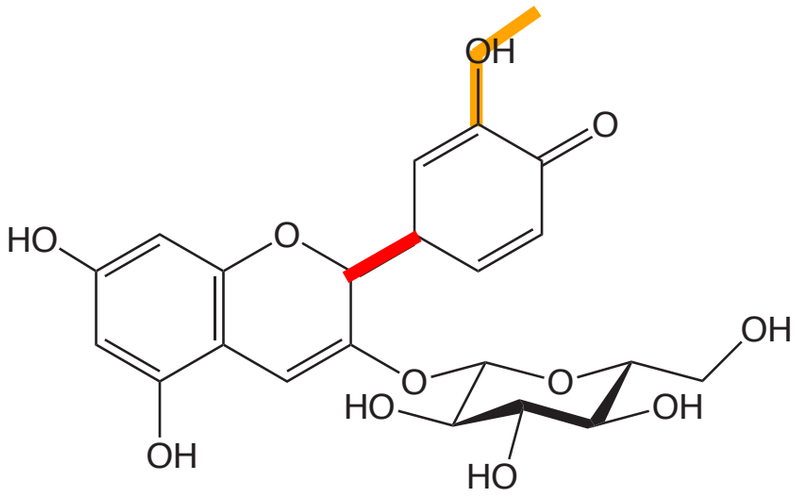


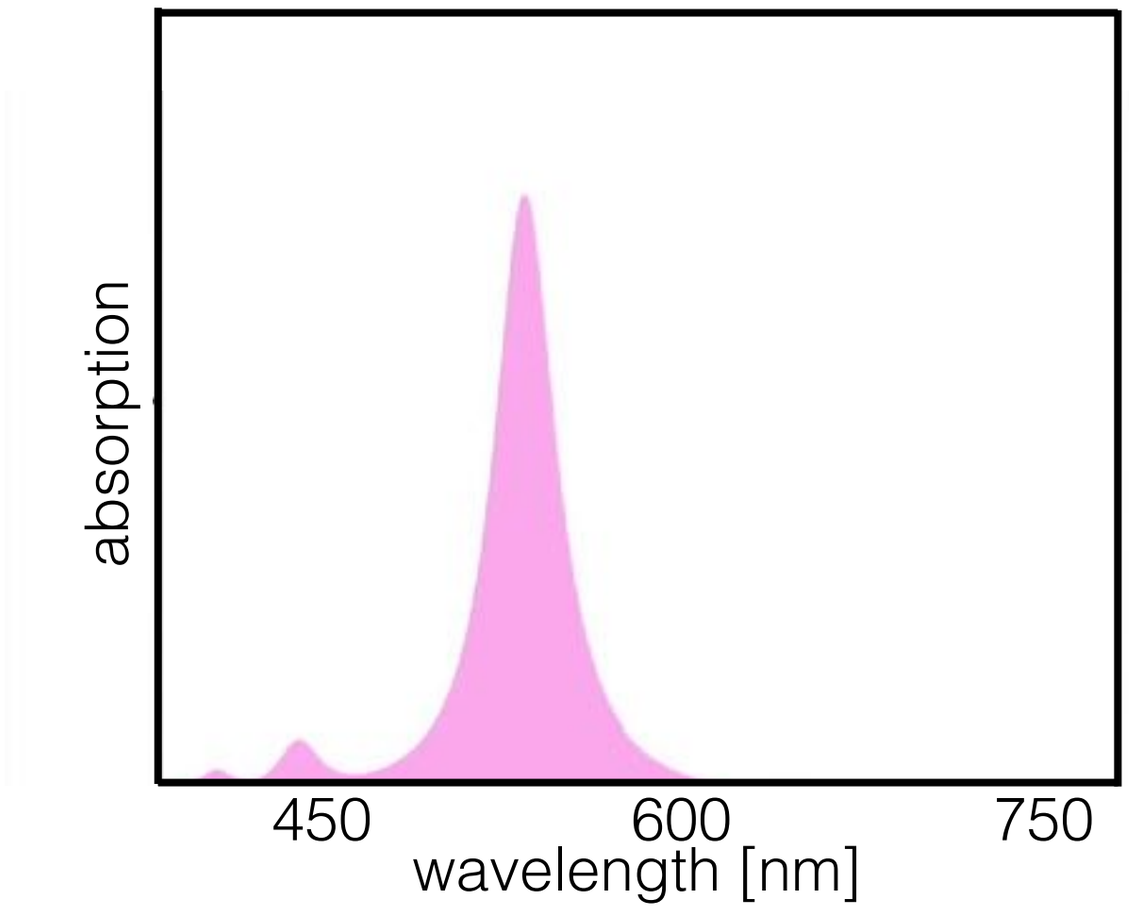




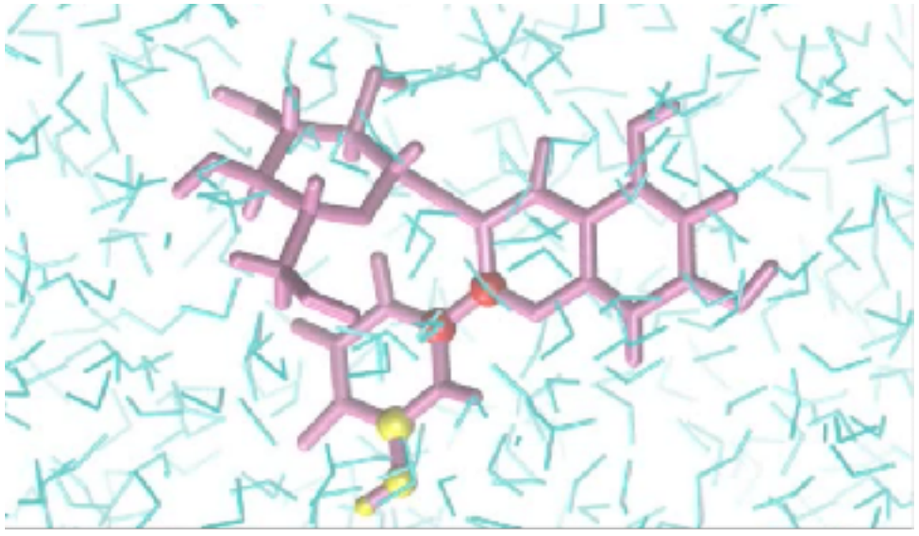
the dance of colors

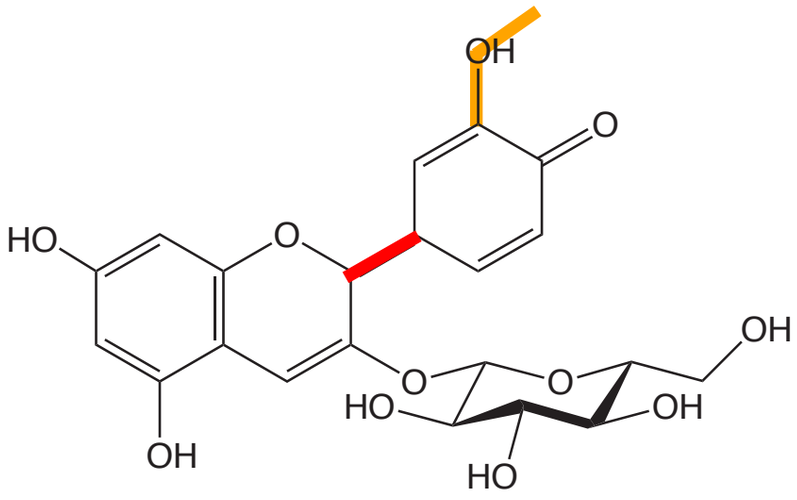


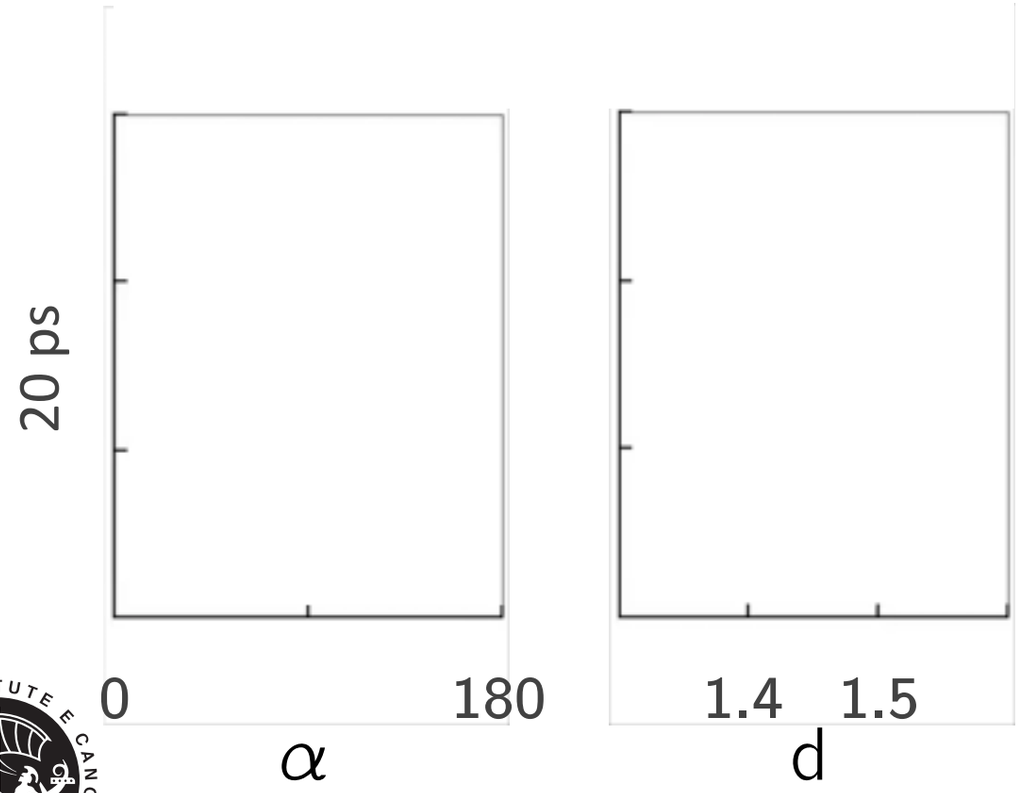


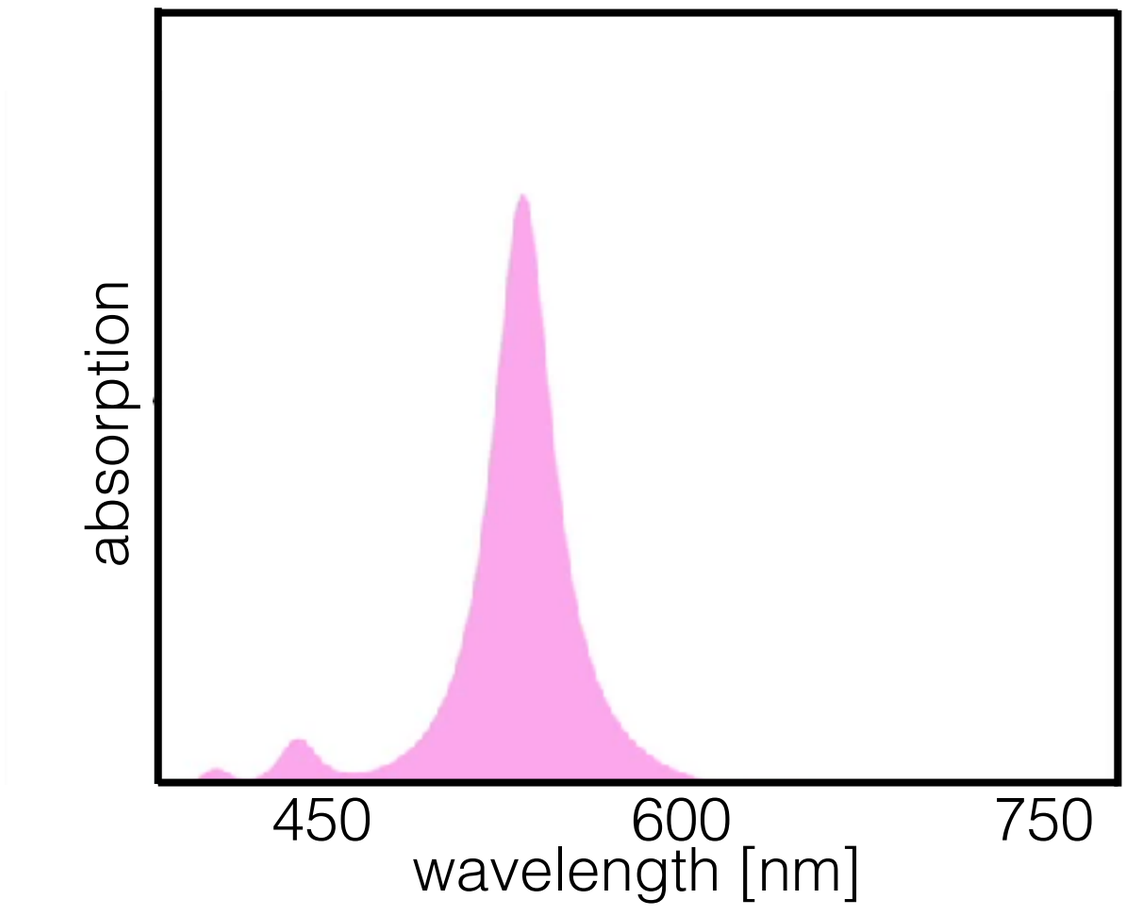


the dance of colors

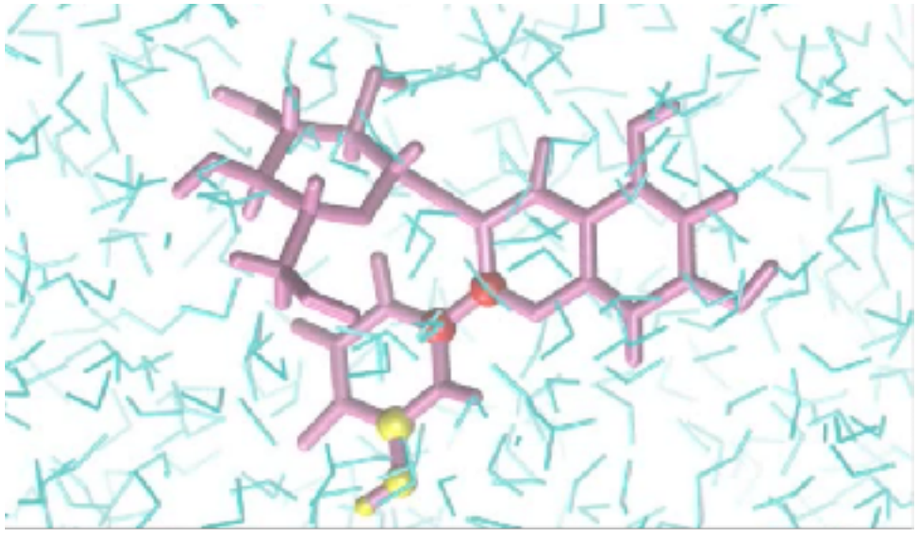


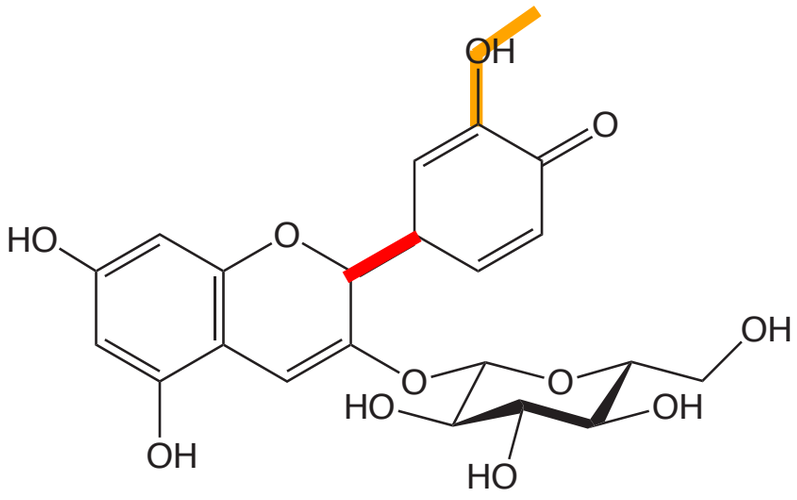


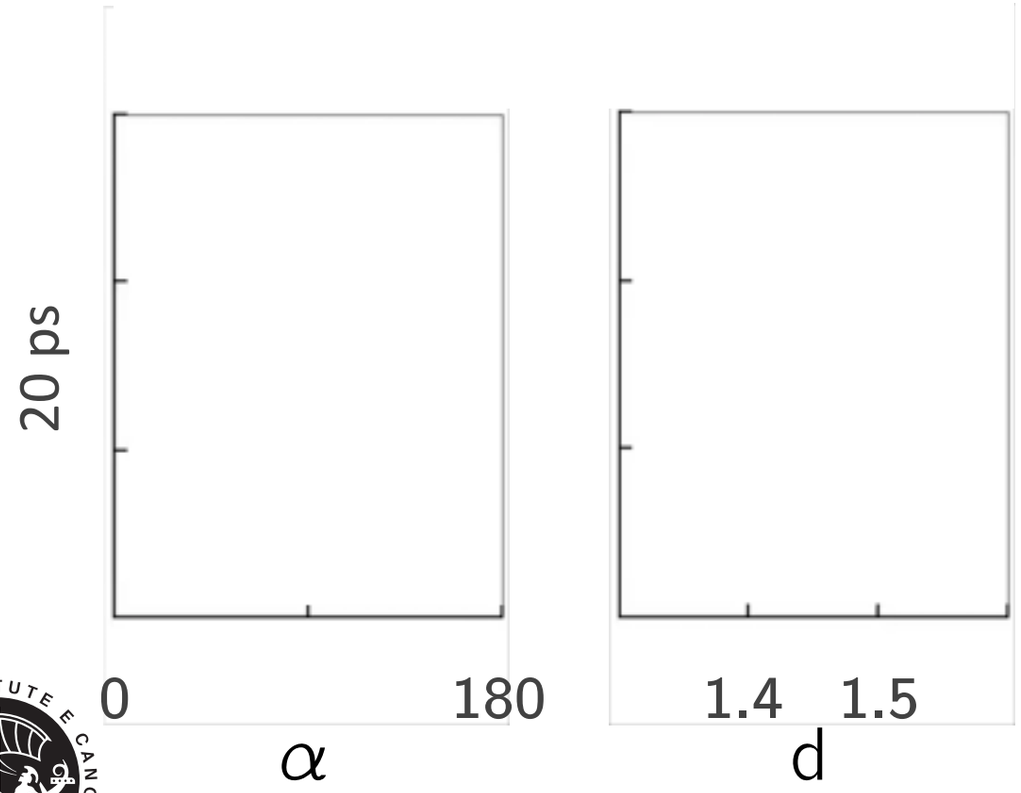


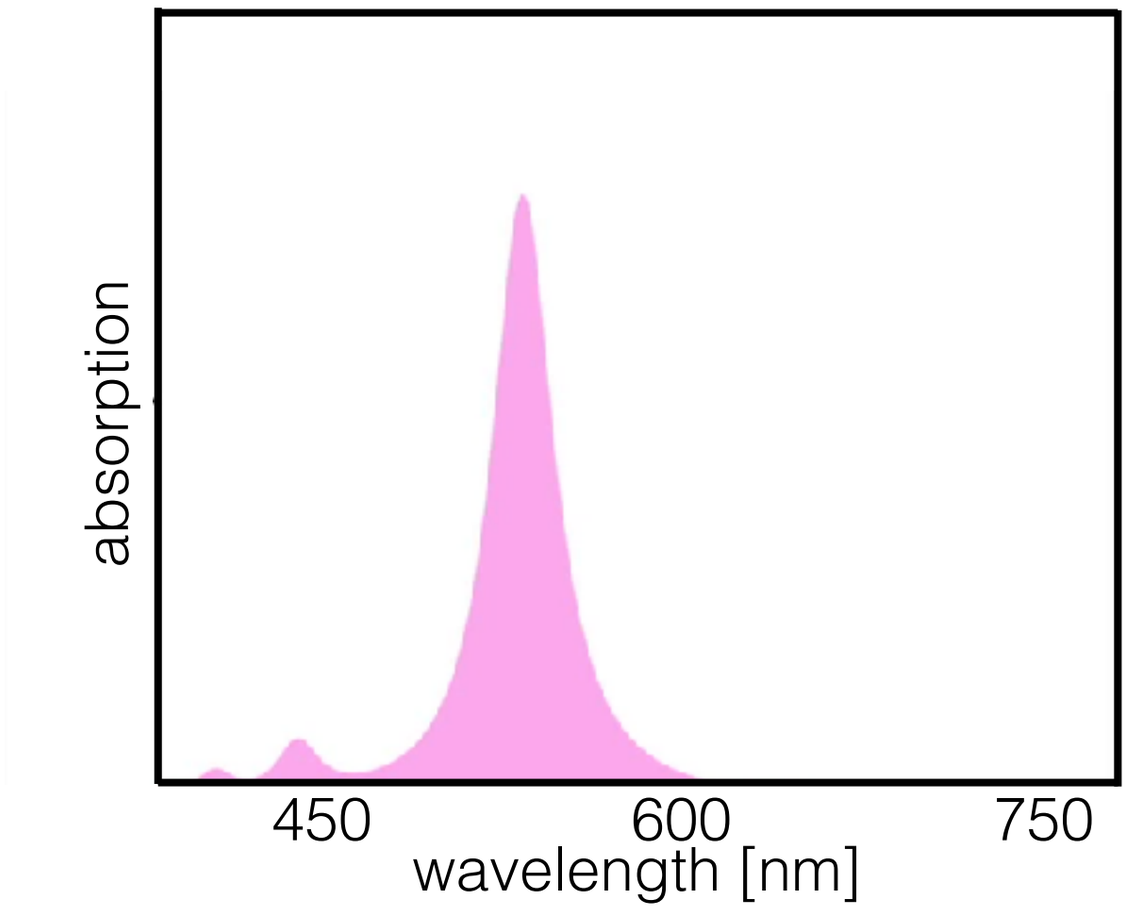


the dance of colors

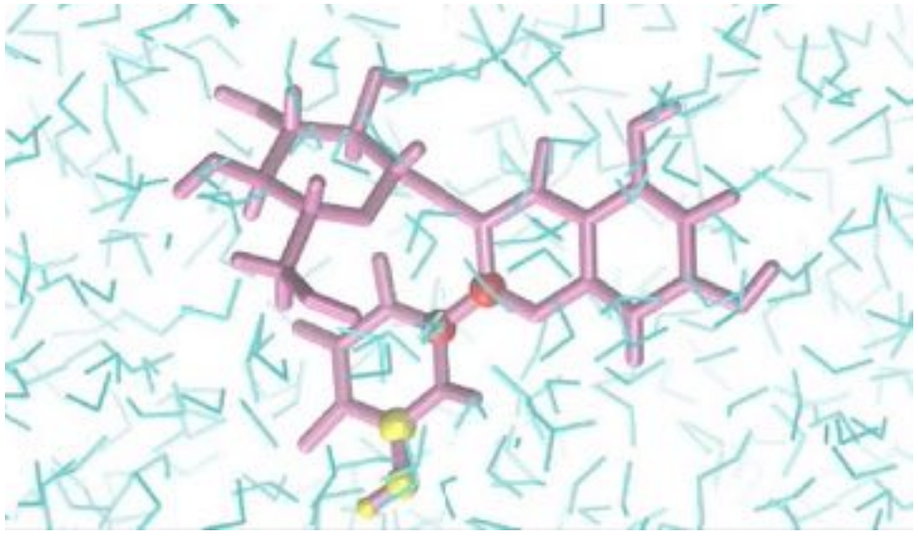


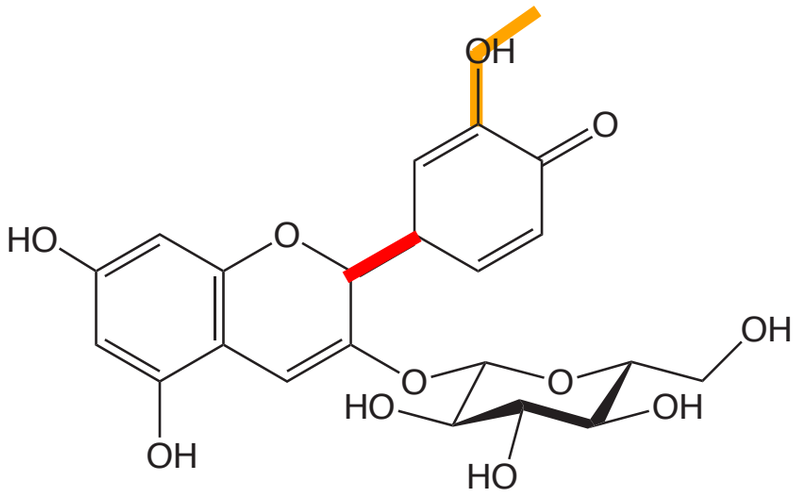


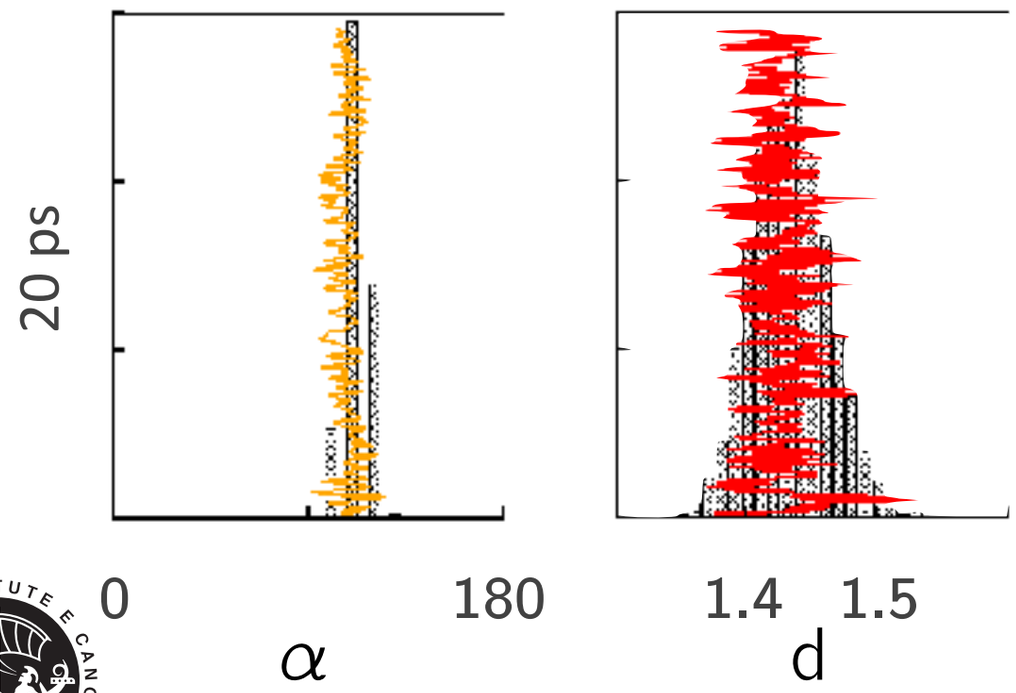


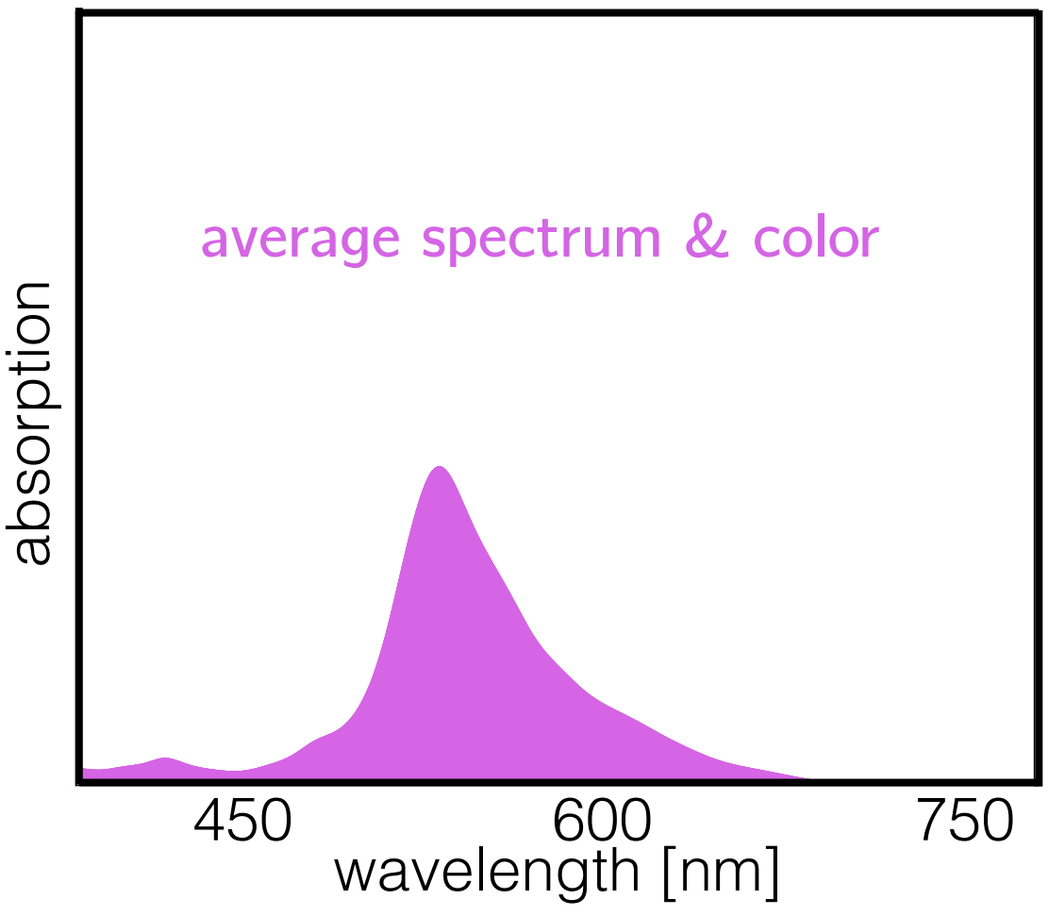


the dance of colors

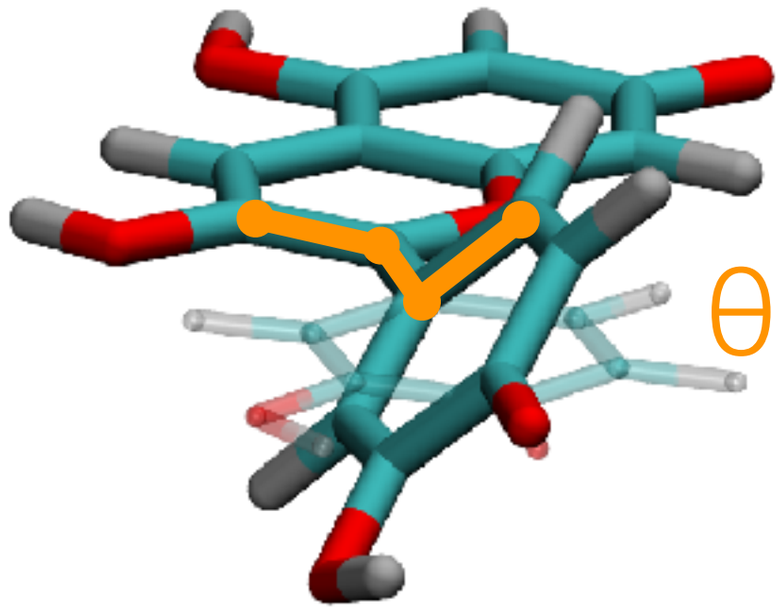








making sense of it



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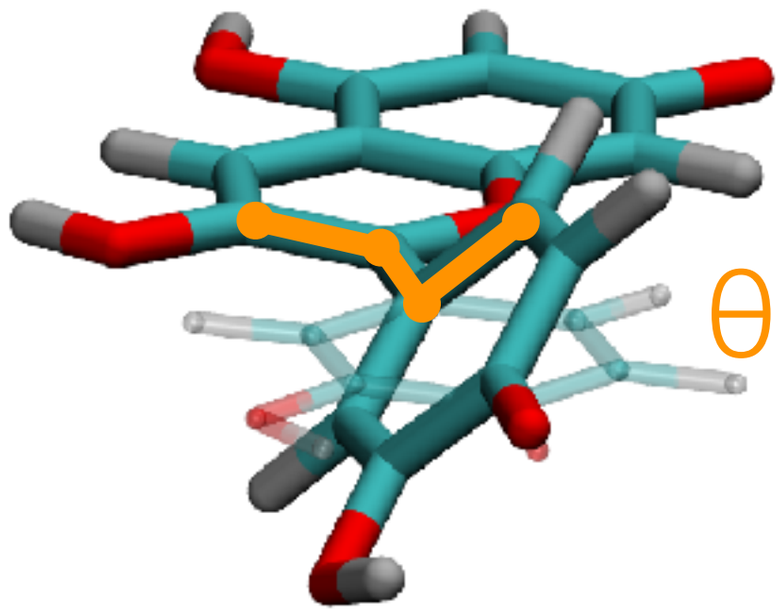

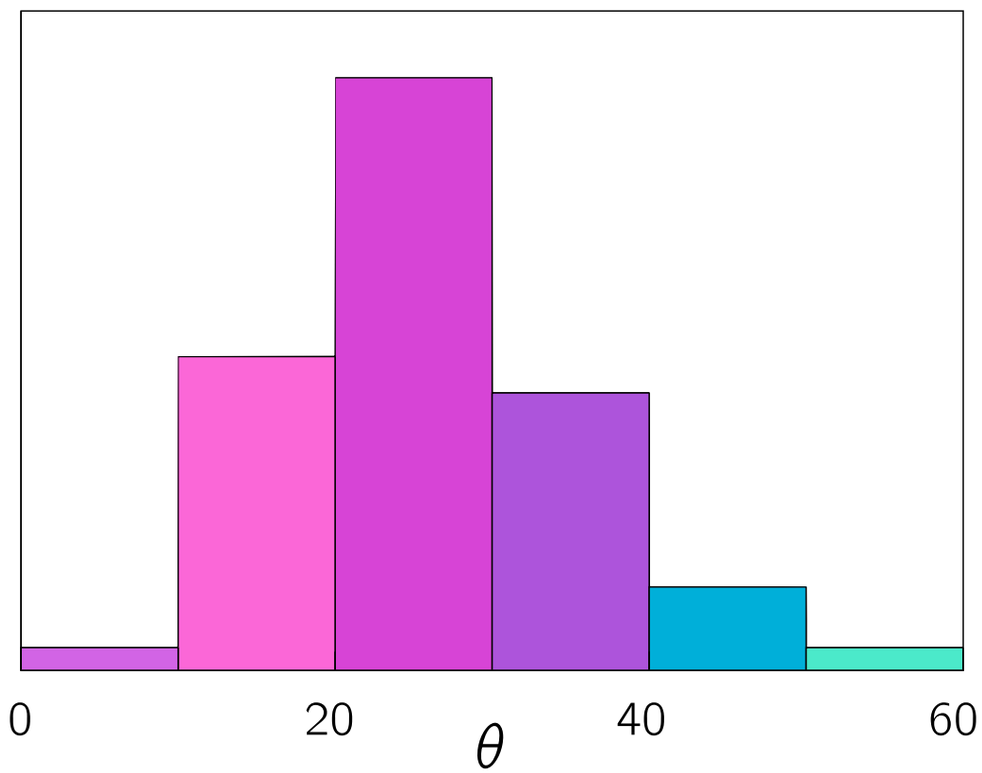

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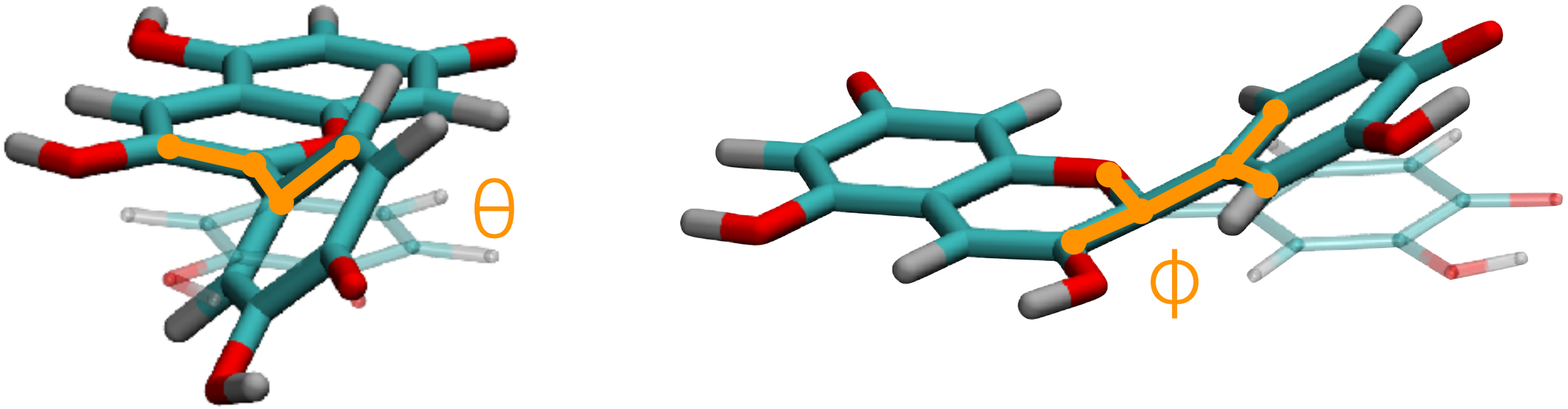
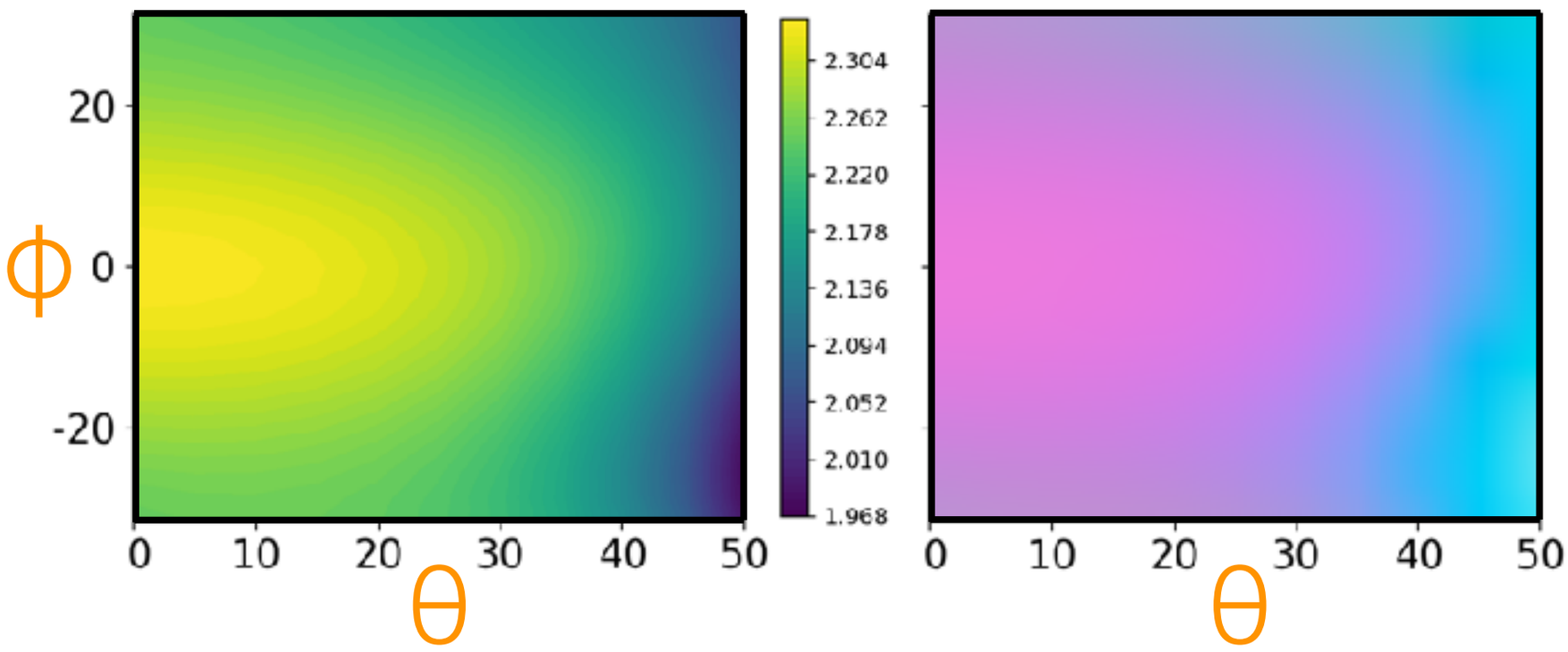
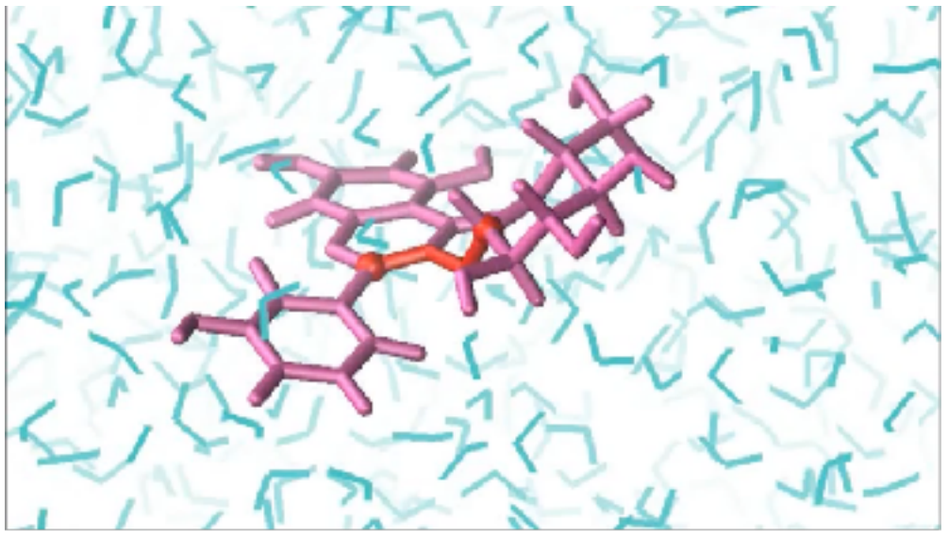


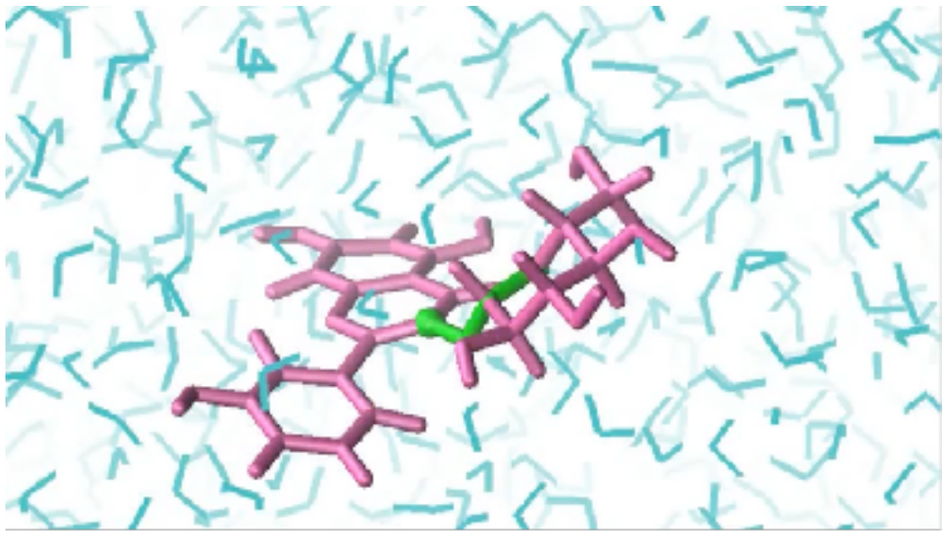
optical gap [eV]

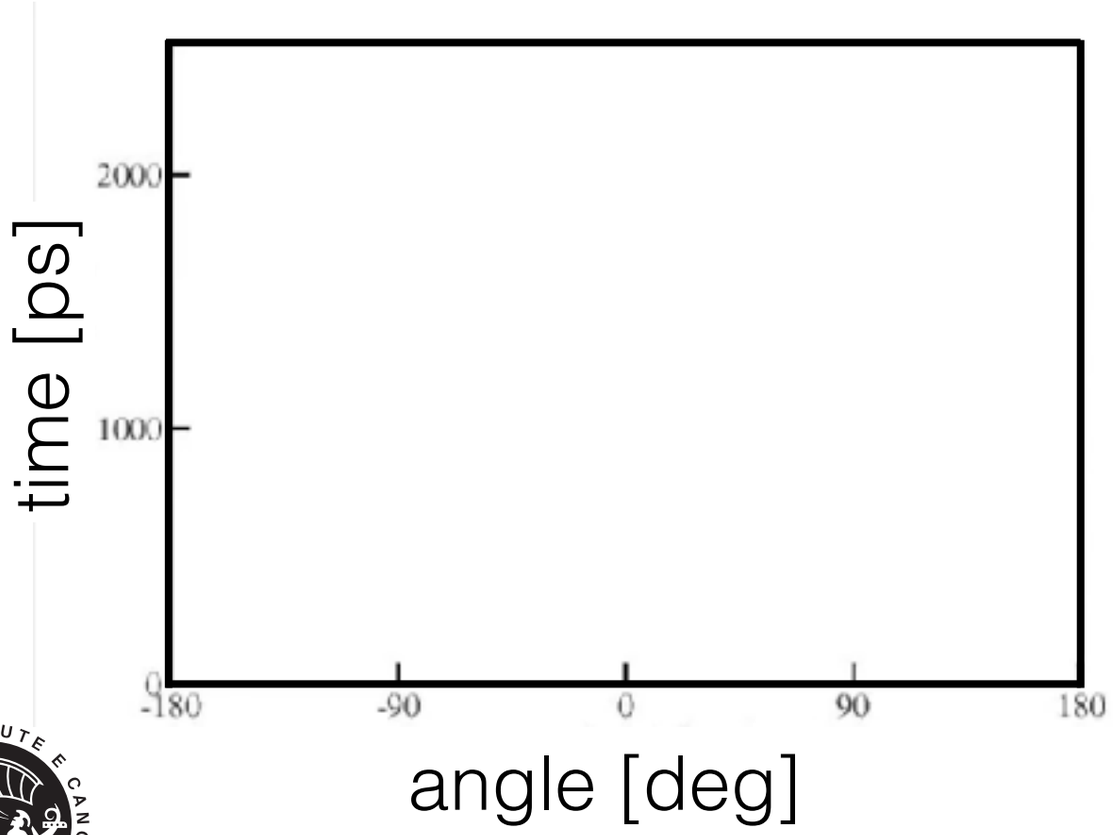


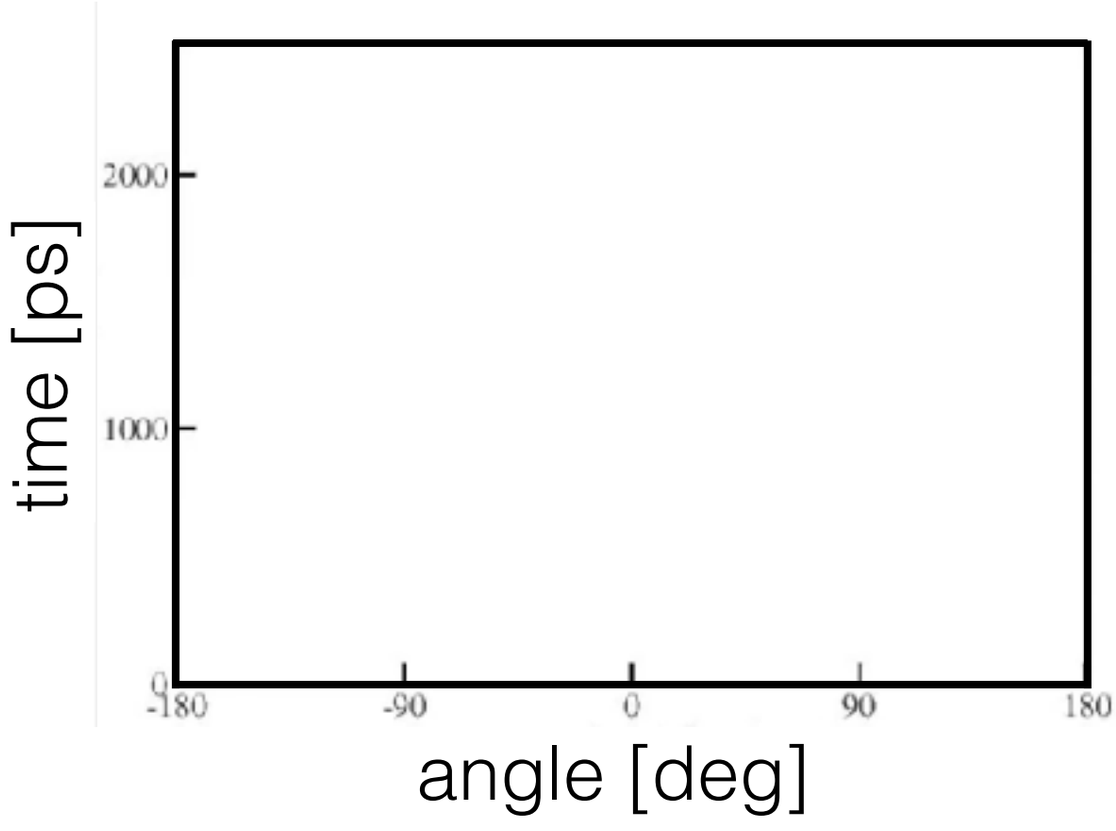
color

why multiscale









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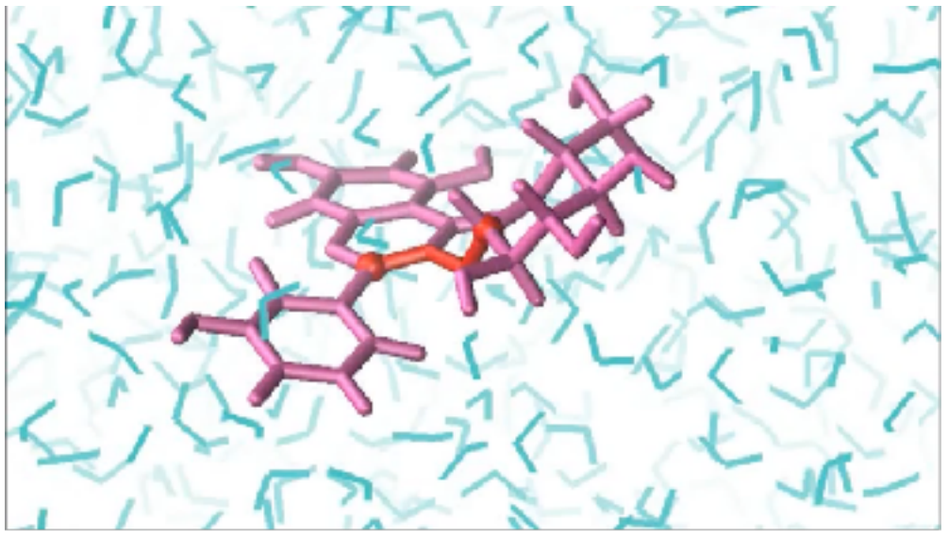

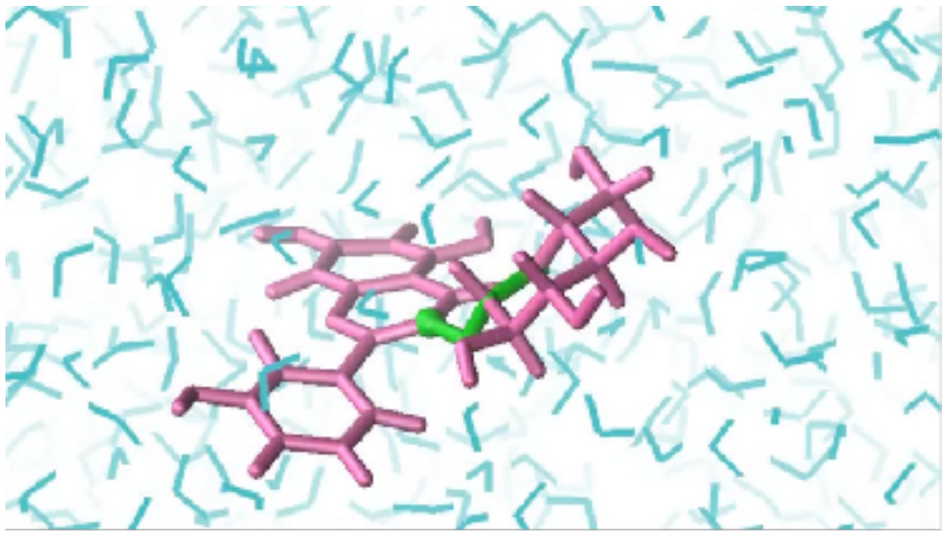

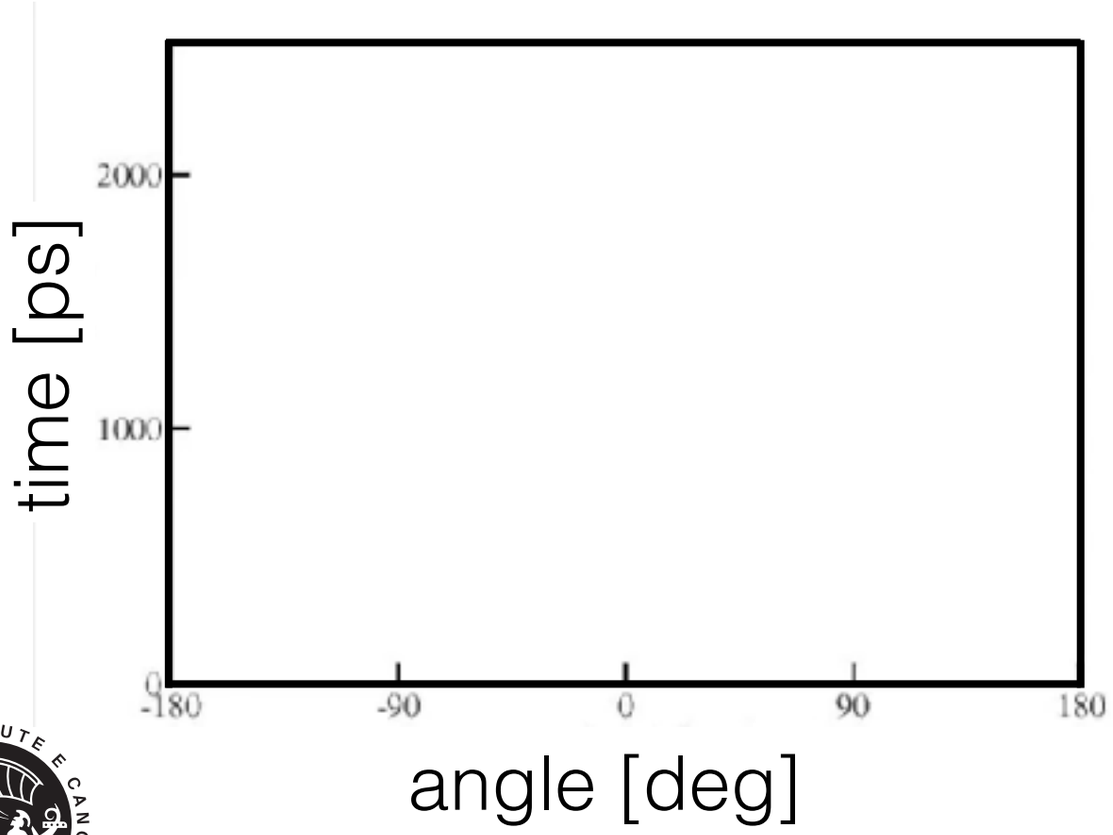

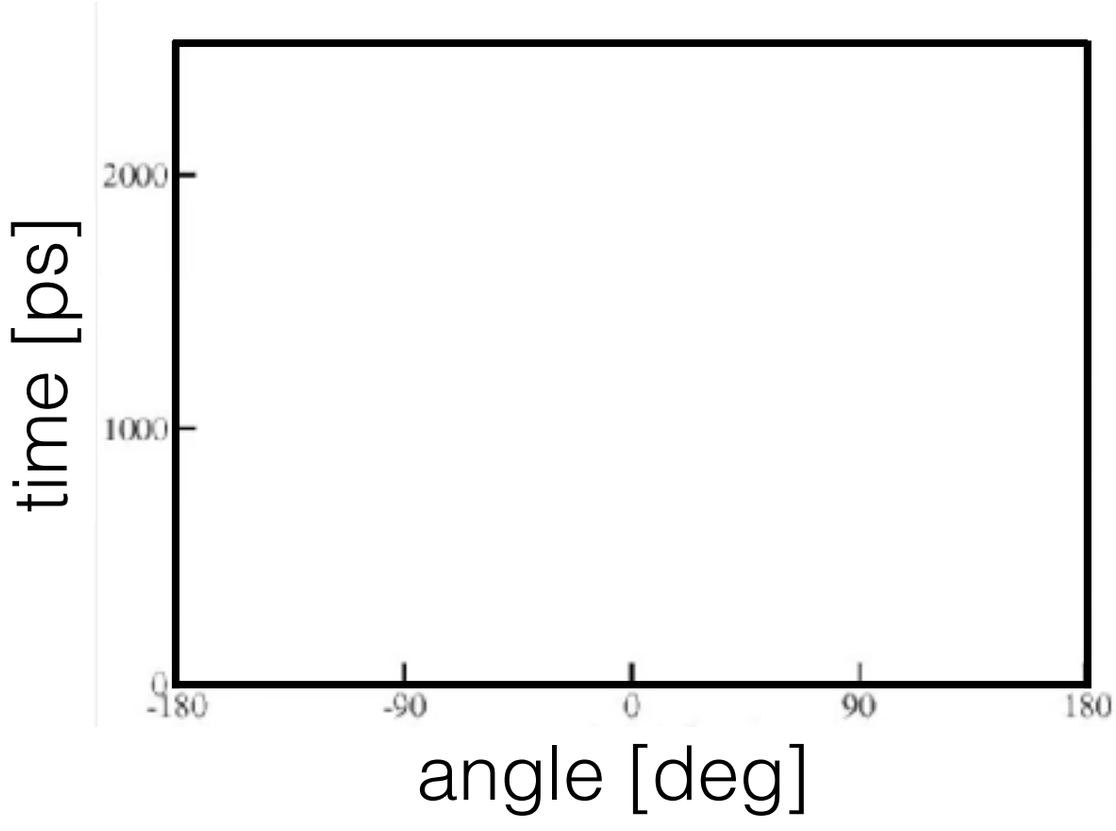

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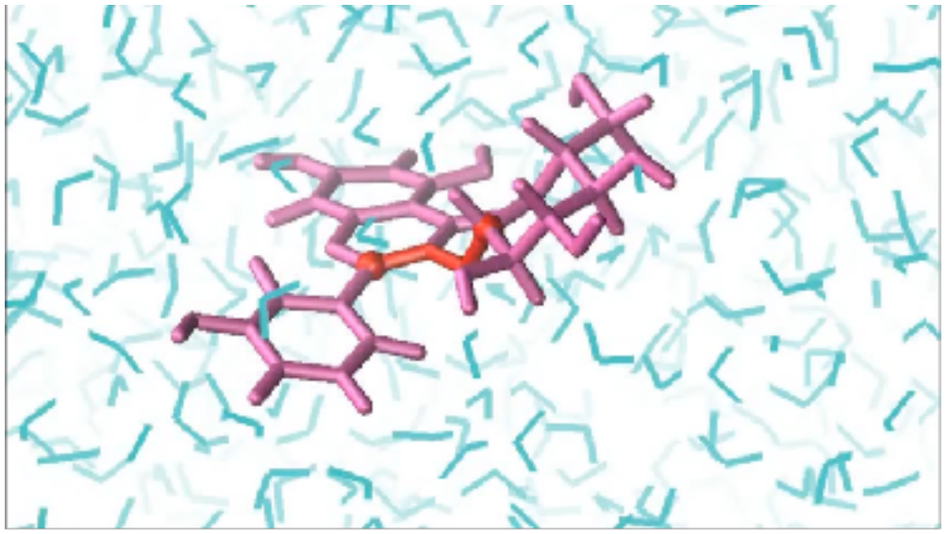
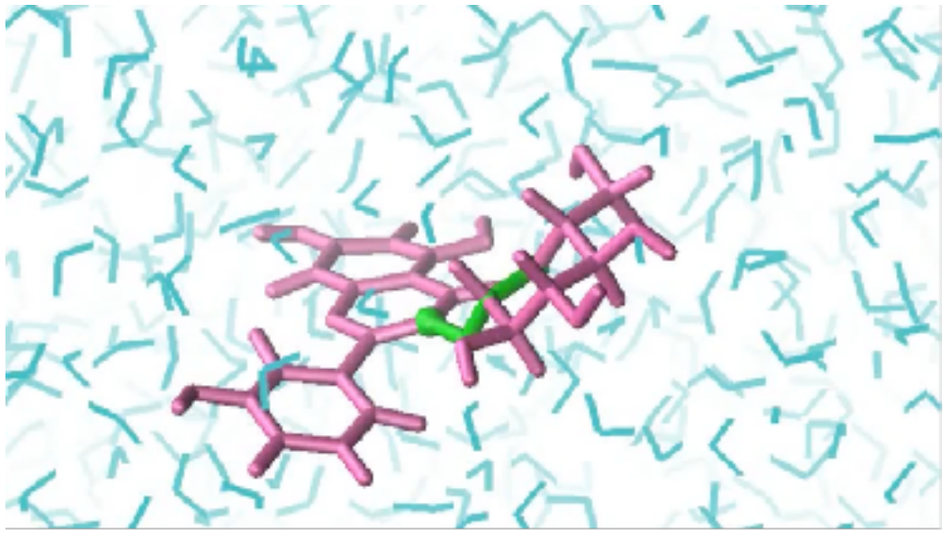
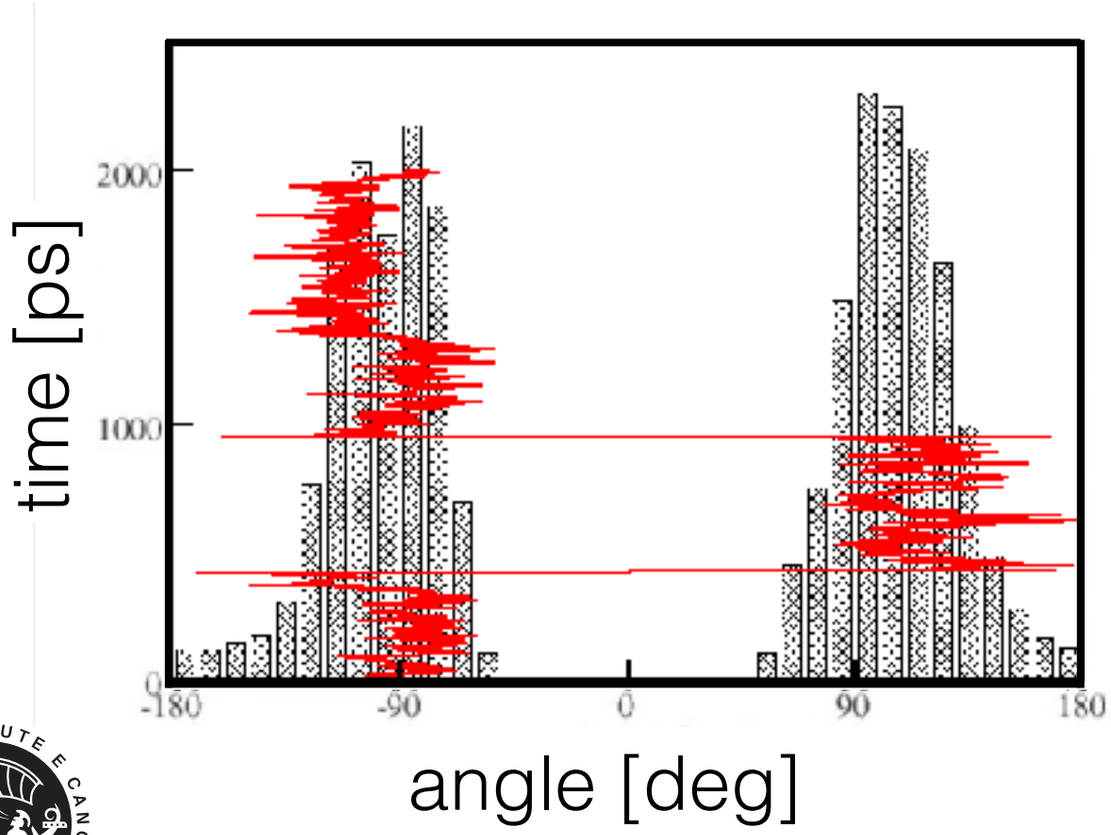
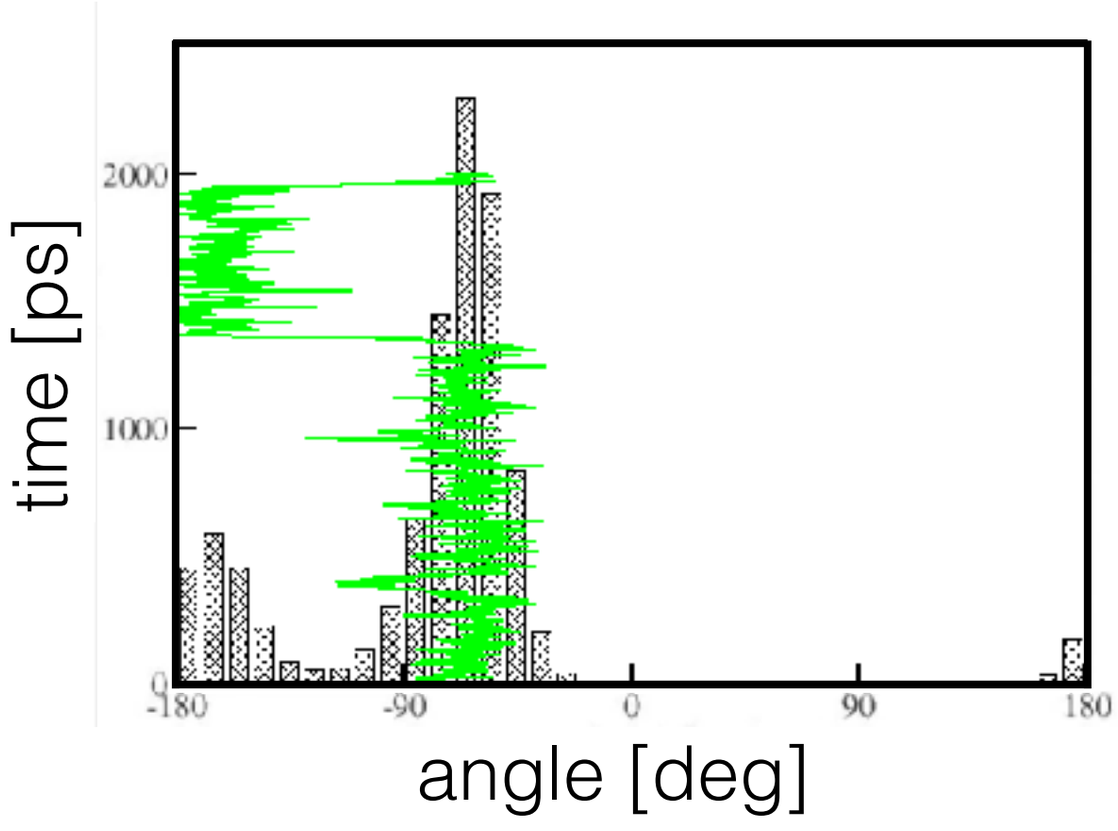


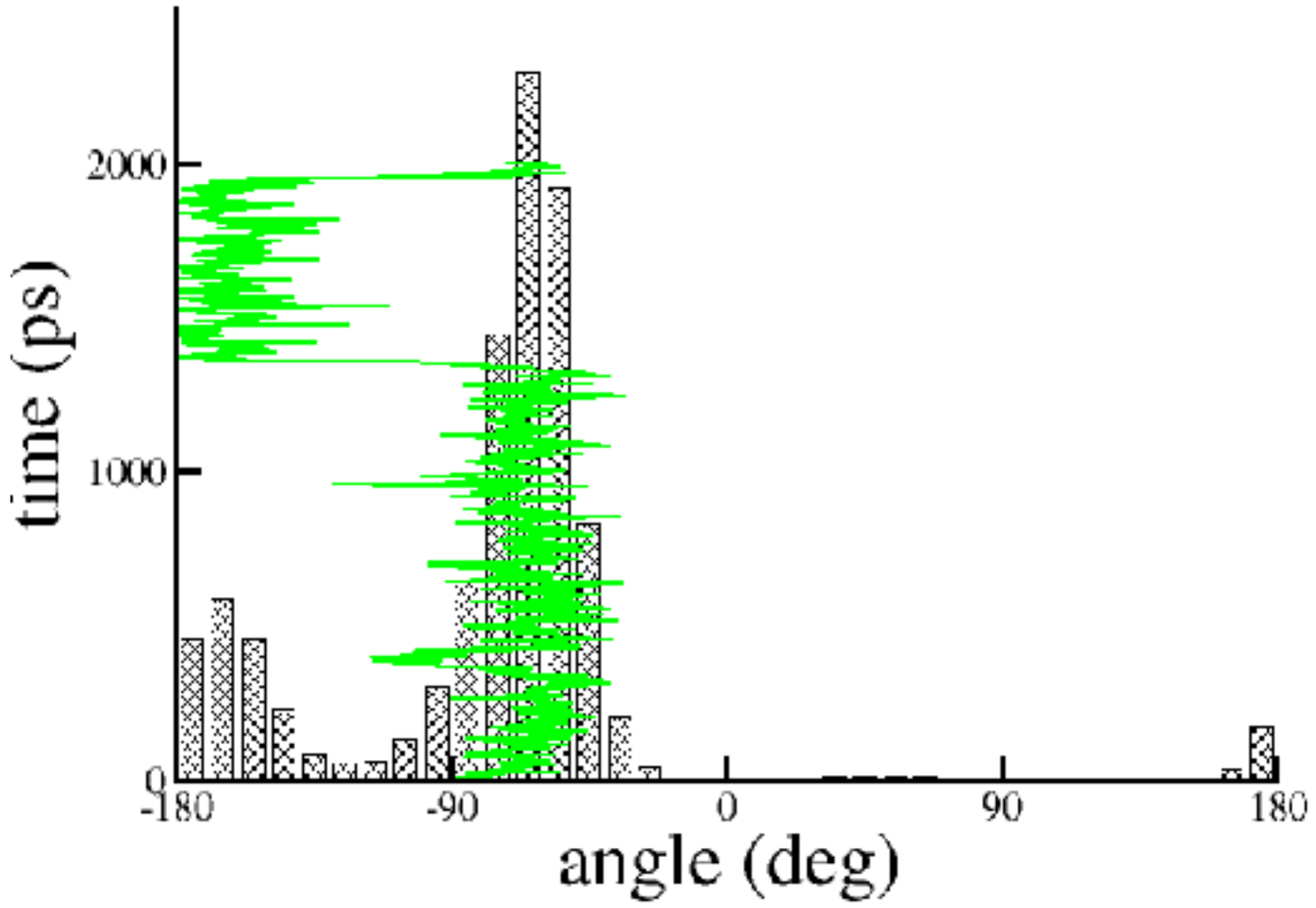






long-time dynamics & statistics

$$\bar{\kappa}(\omega) \approx \frac{1}{T} \int_0^T \kappa(\omega, \mathbf{R}(t)) dt$$



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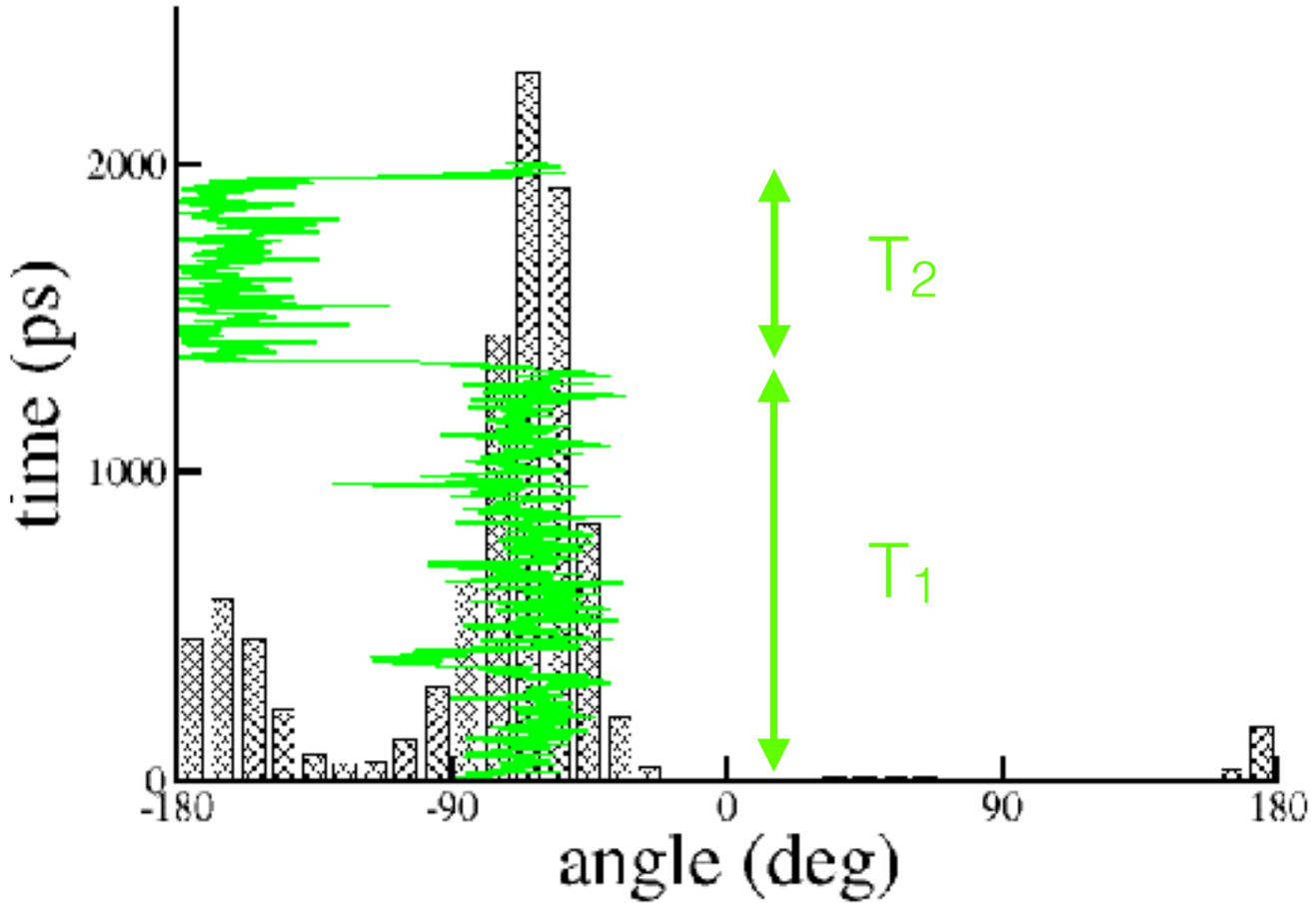

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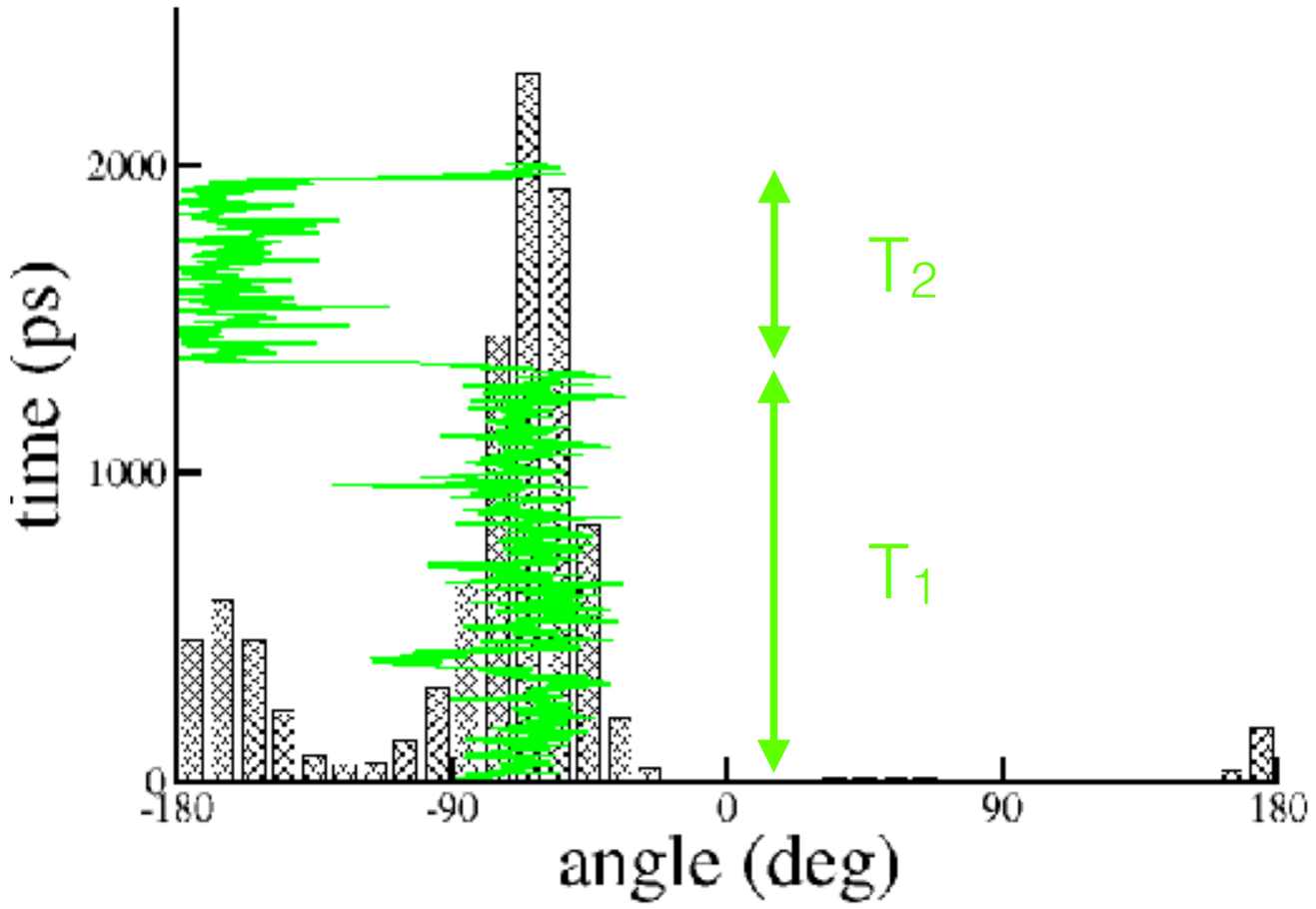
$$= \frac{T_1}{T}\frac{1}{T_1}\int_0^{T_1} \kappa(\omega, \mathbf{R}(t))dt + \frac{T_2}{T}\frac{1}{T_2}\int_0^{T_2} \kappa(\omega, \mathbf{R}(t))dt + \cdots$$



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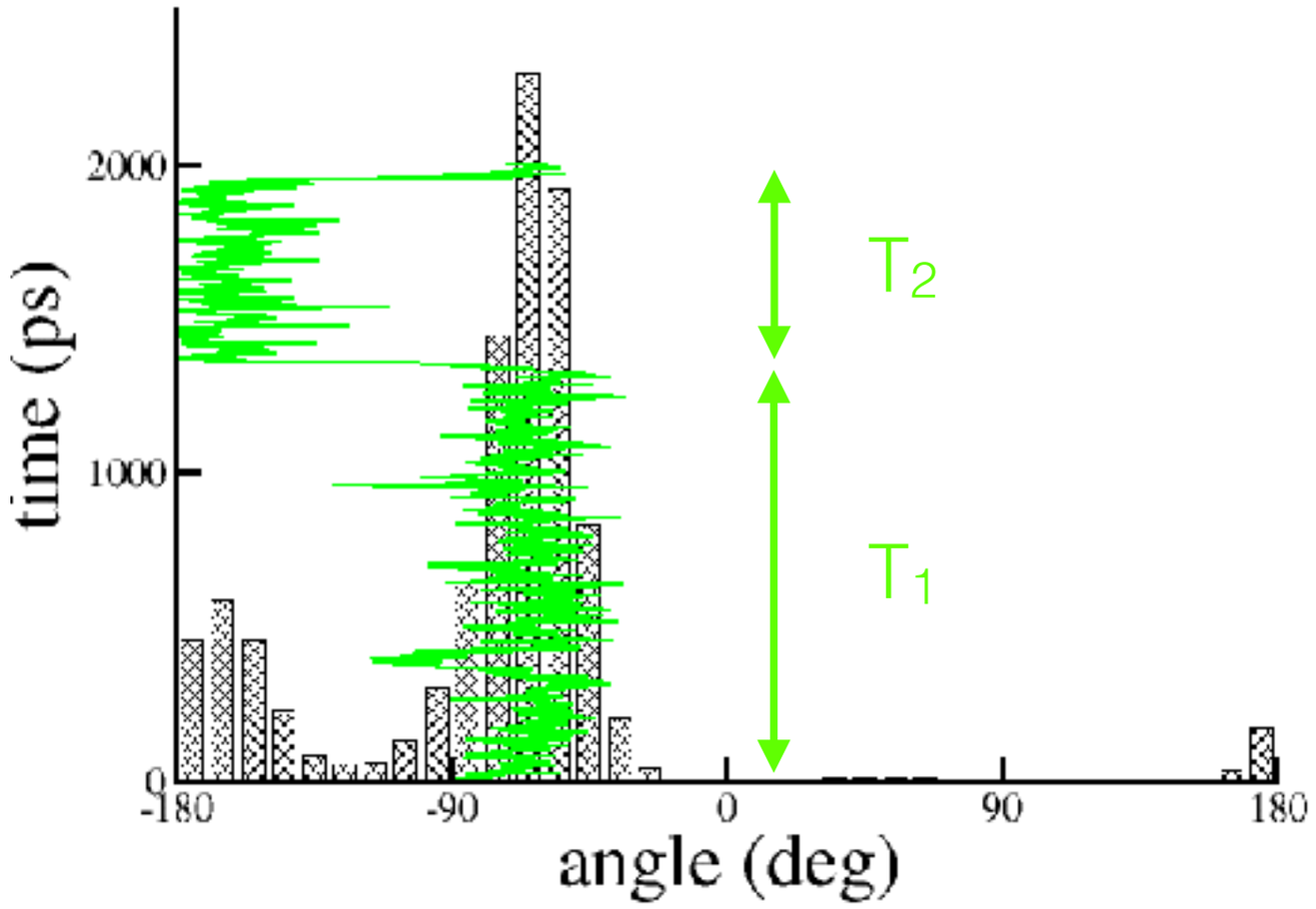
$$\sim \sum_c p_c \, \frac{1}{T_c}\int_0^{T_c} \kappa(\omega, \mathbf{R}(t))dt$$



long-time dynamics & statistics

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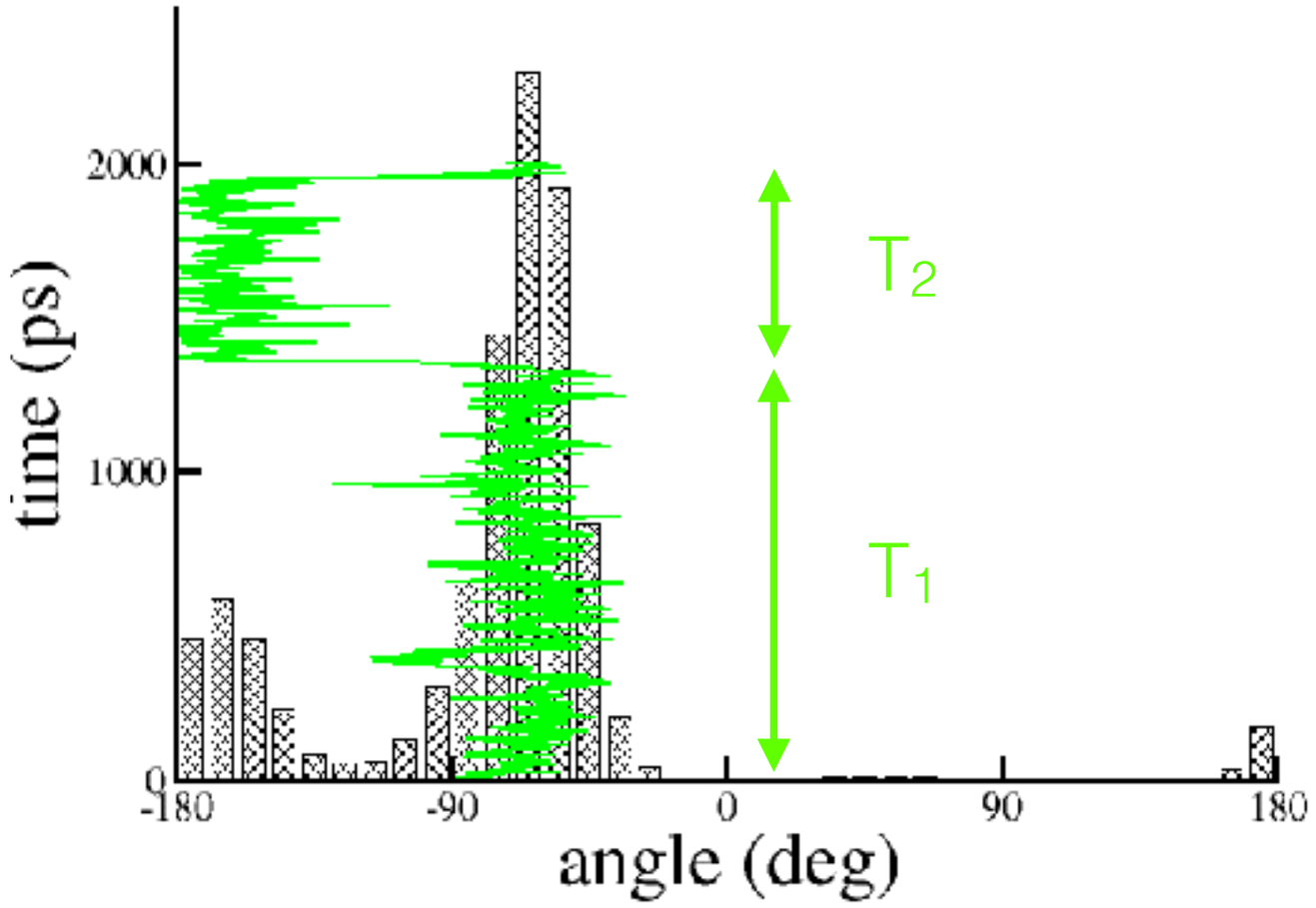
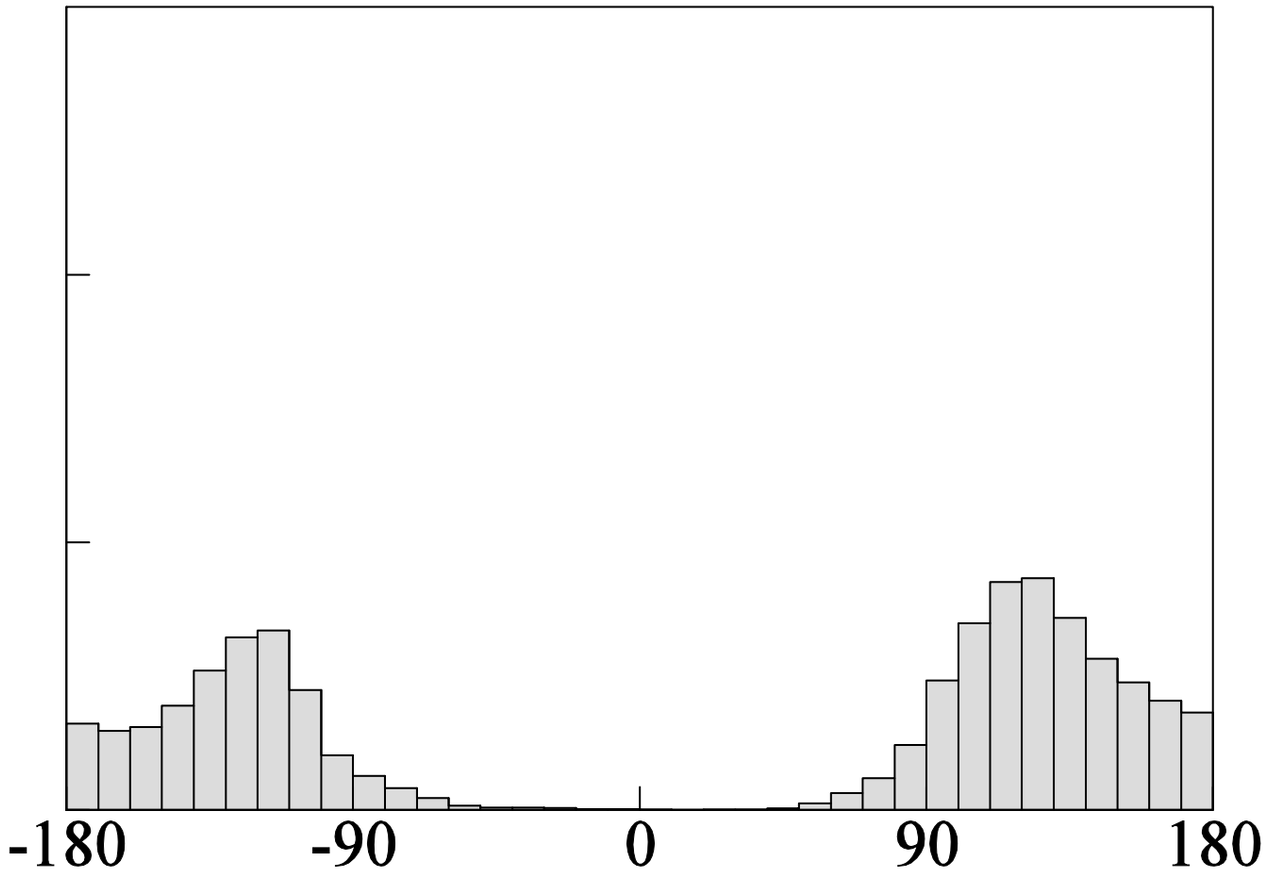
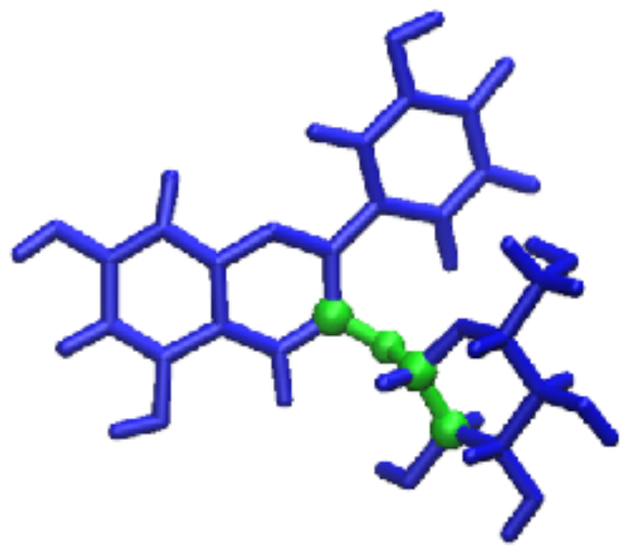


conformational analysis





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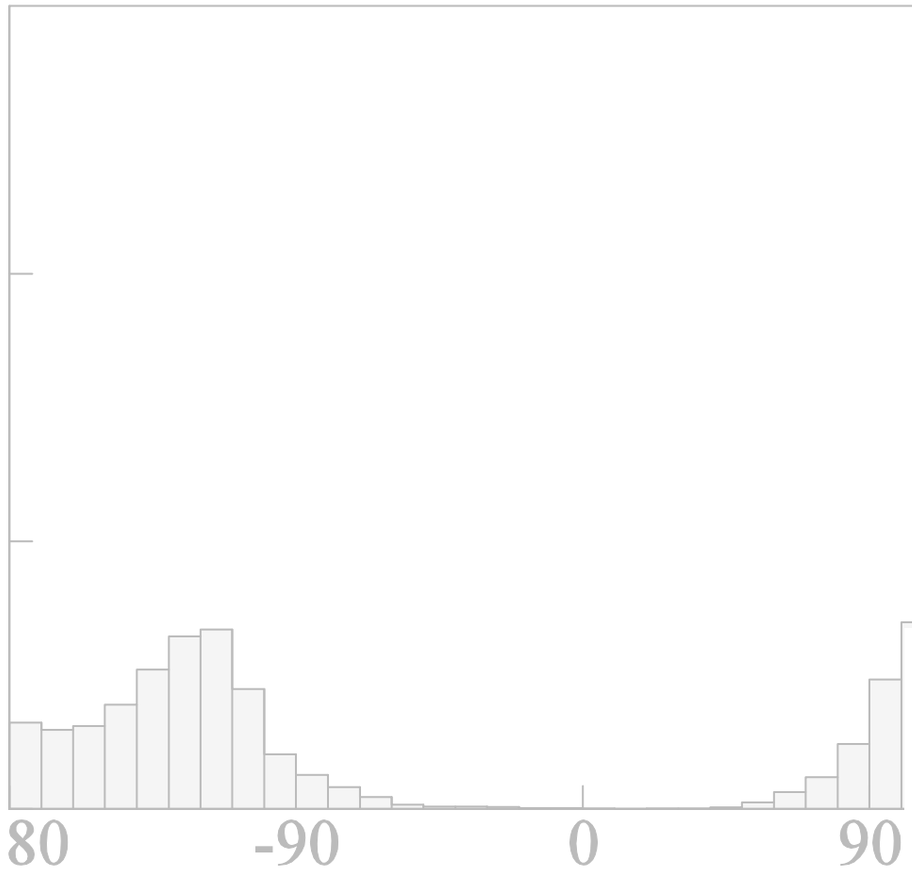

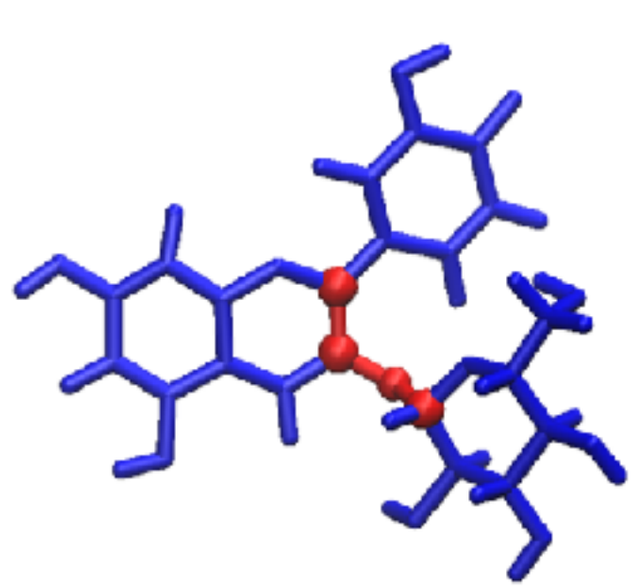

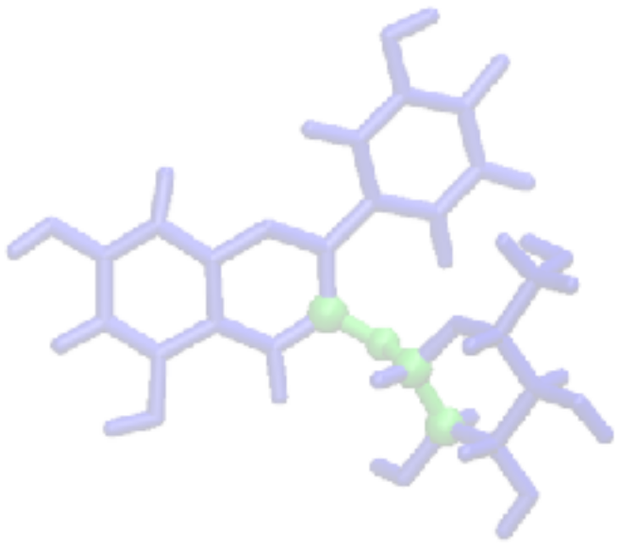

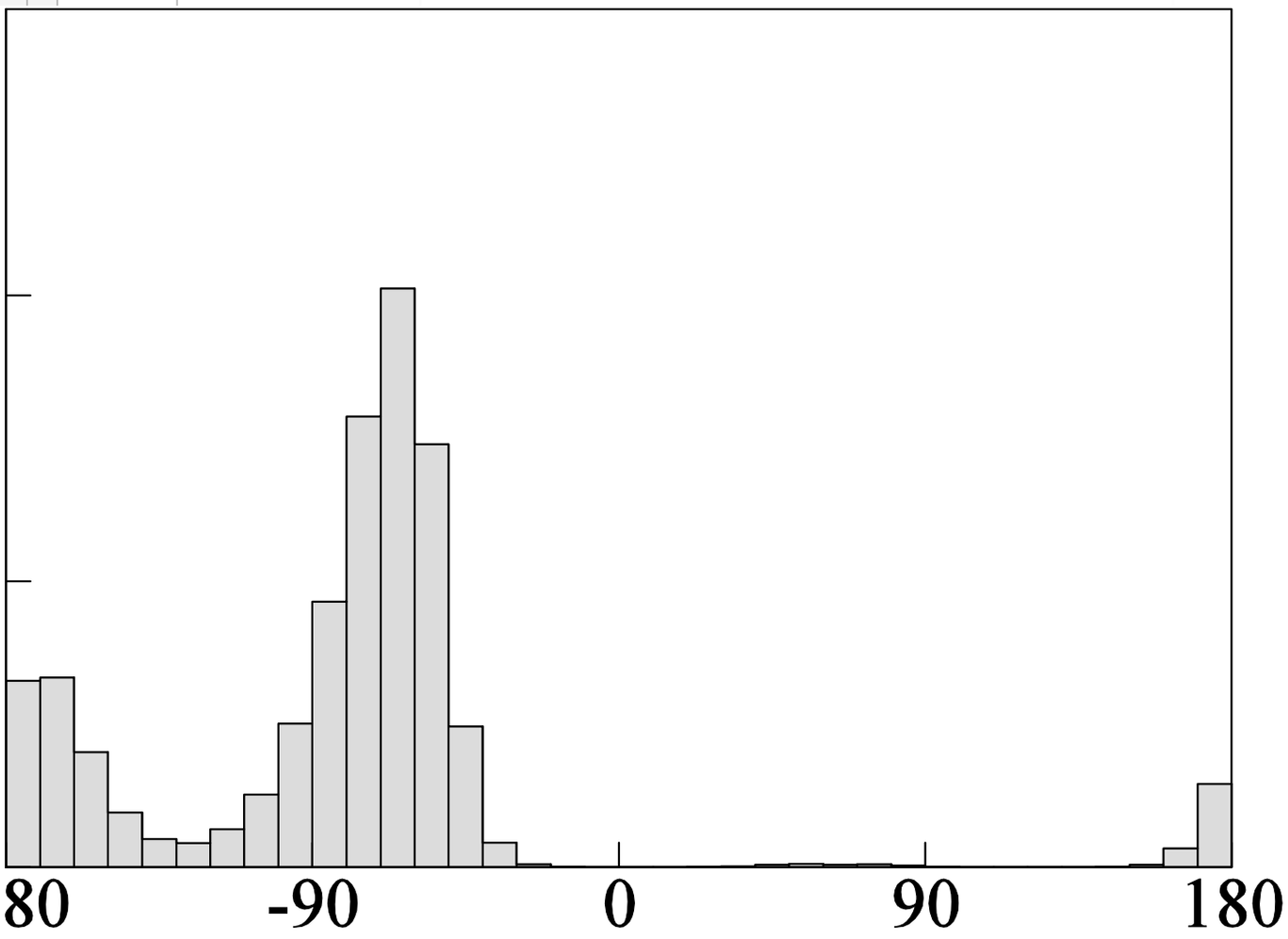

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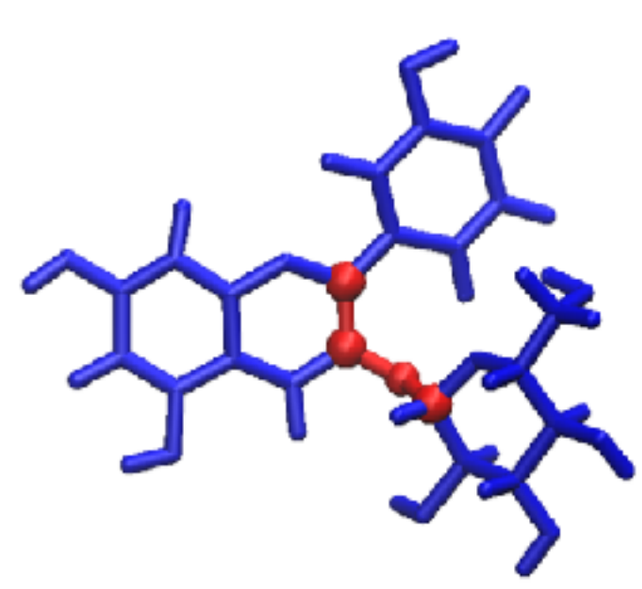

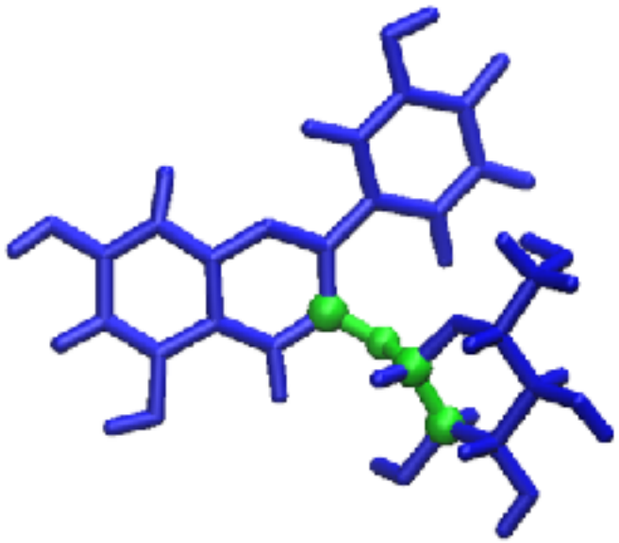

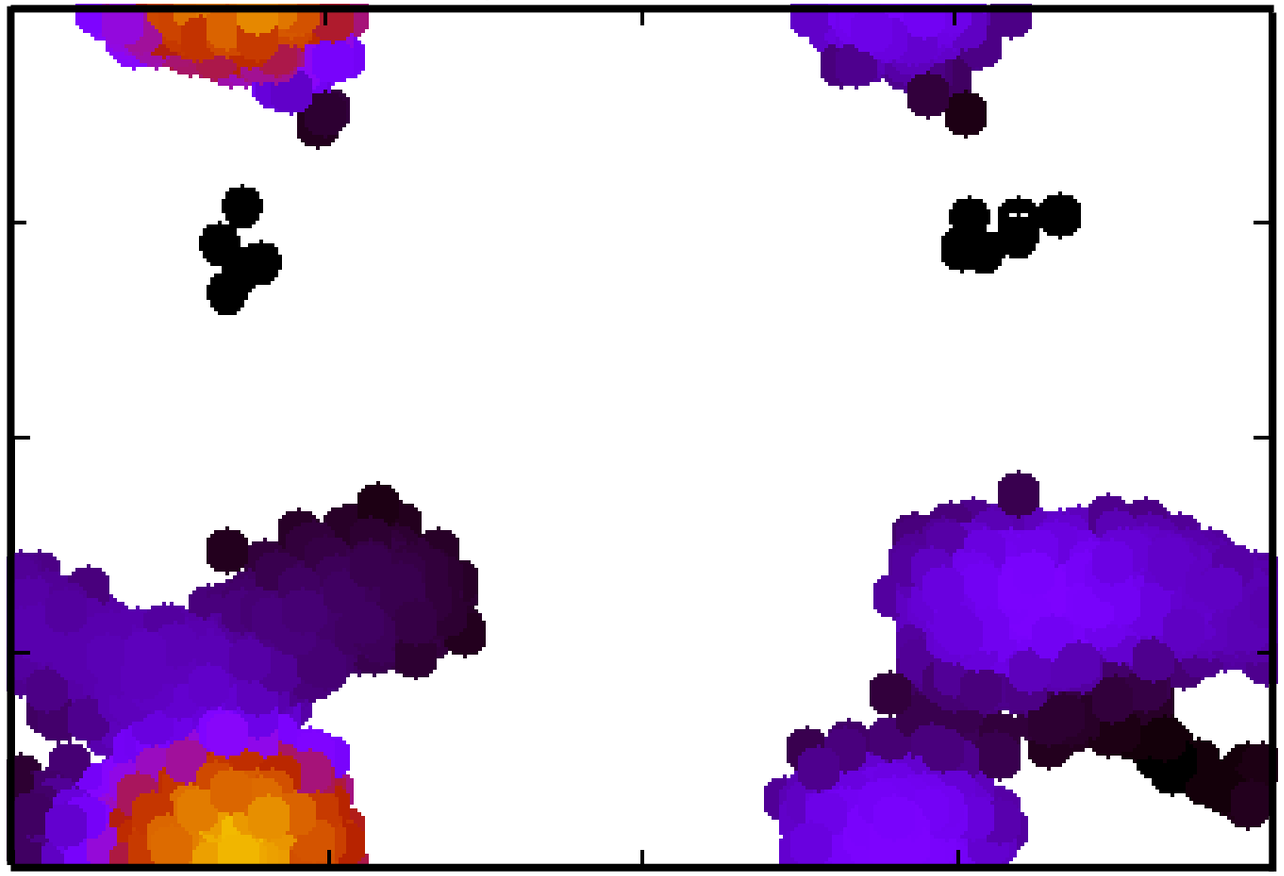

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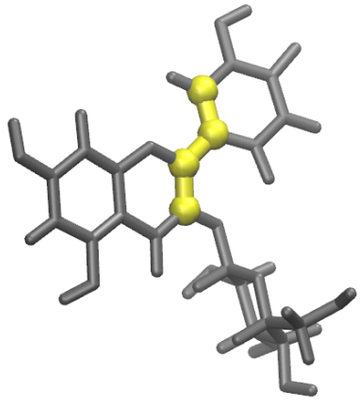

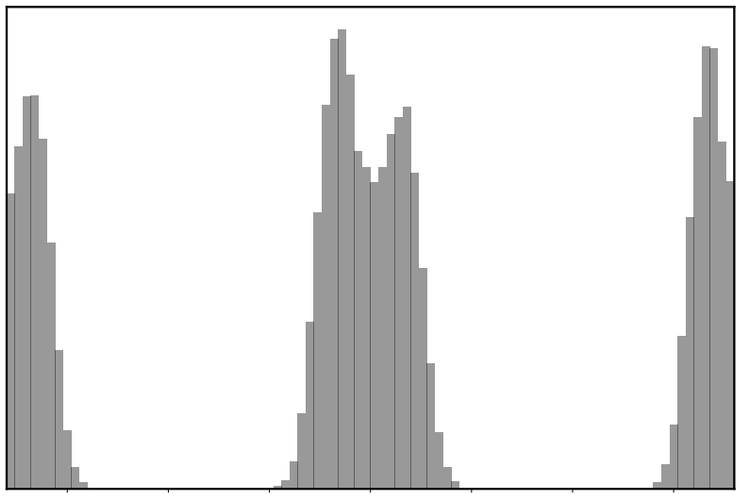

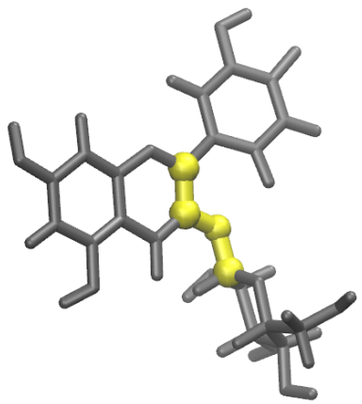

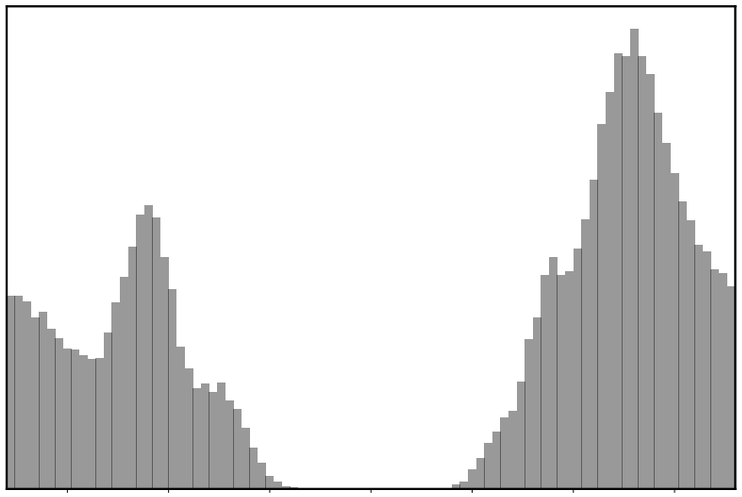

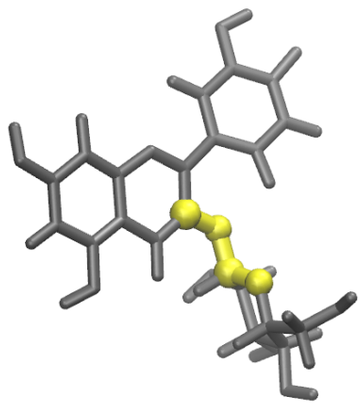

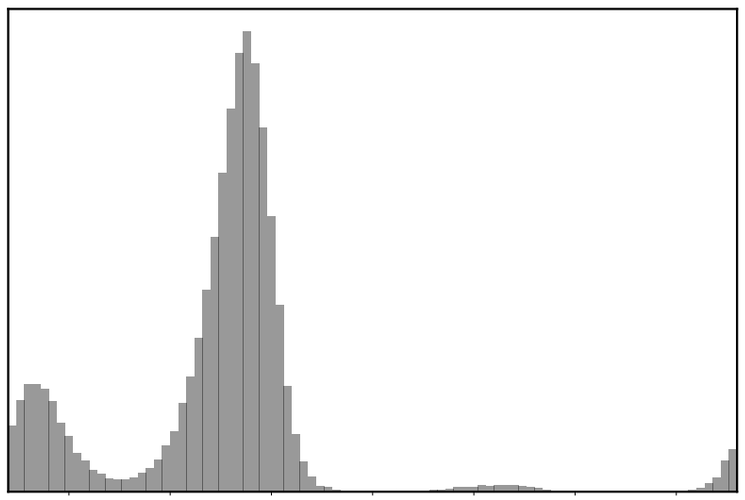

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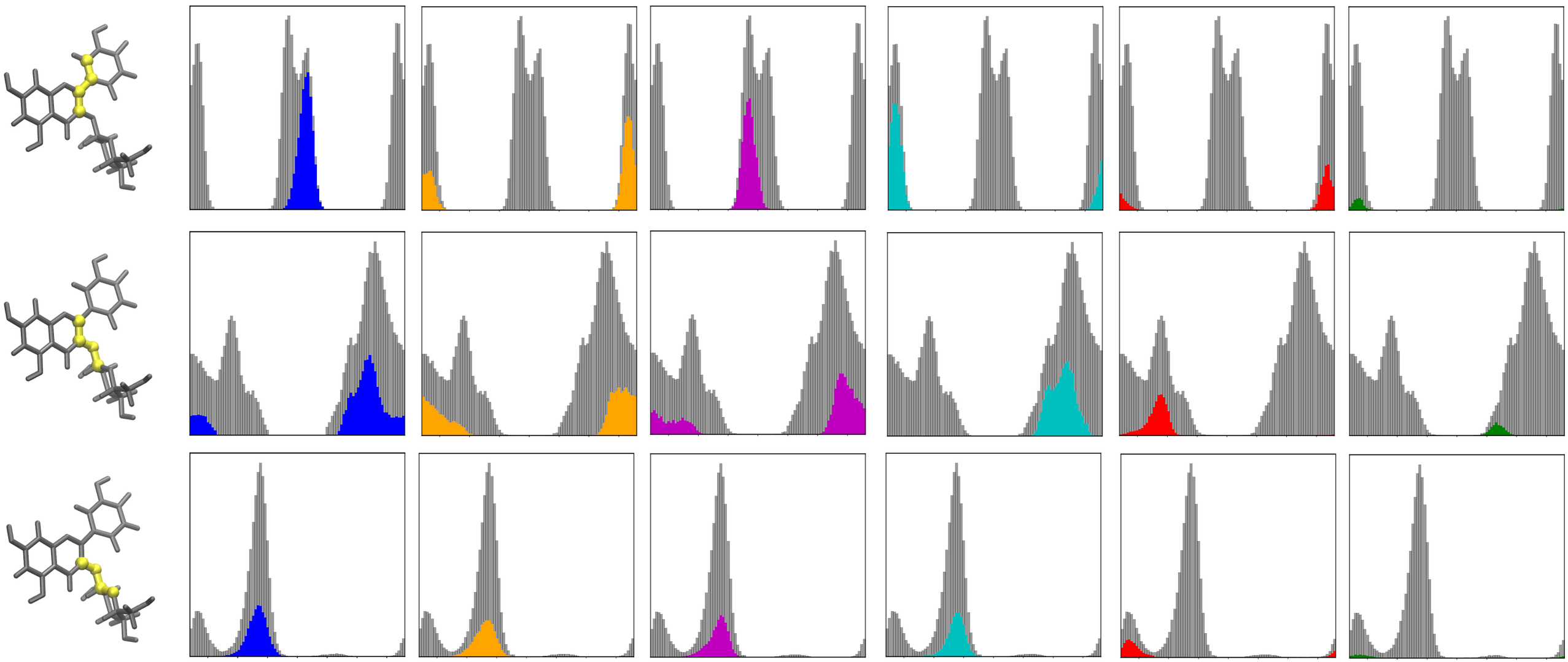

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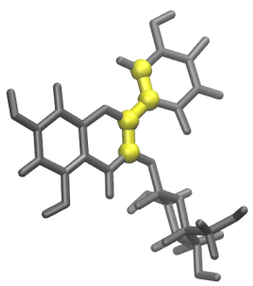
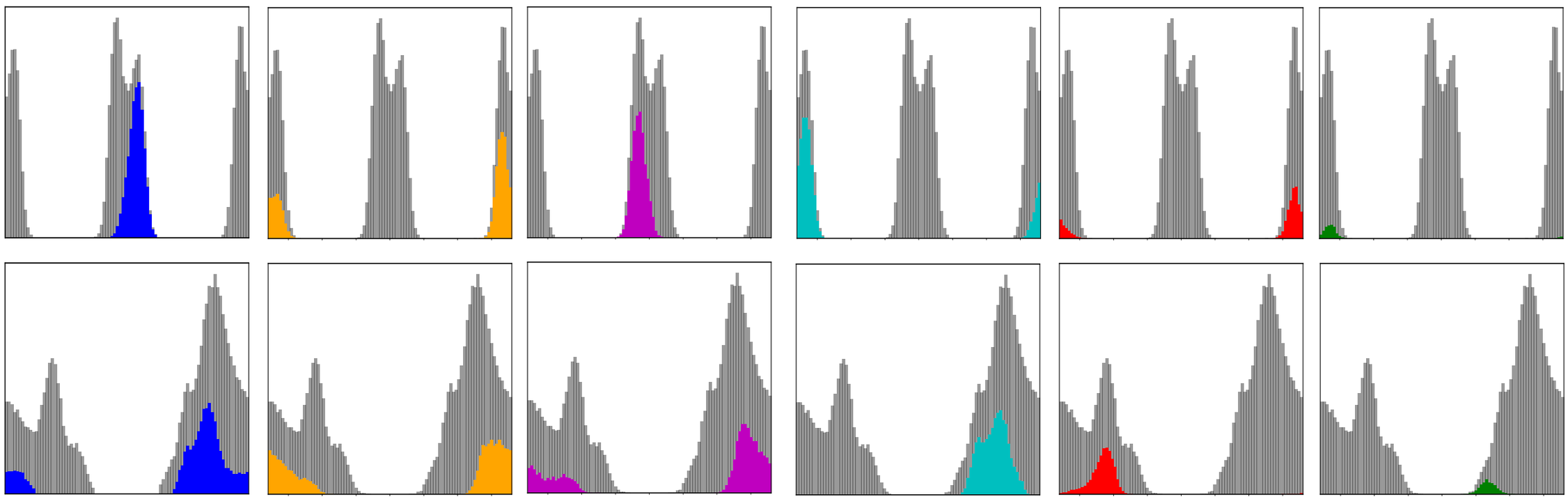
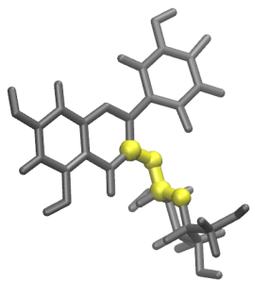
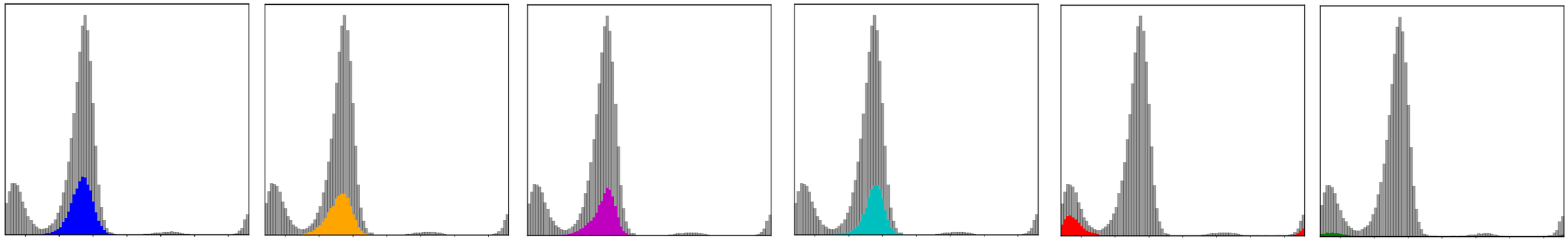
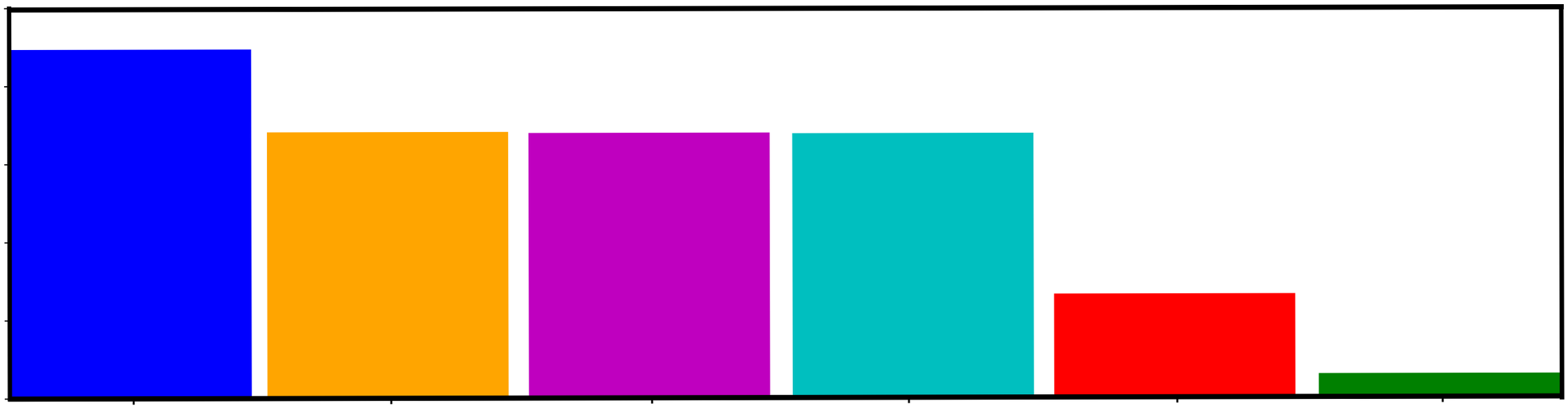
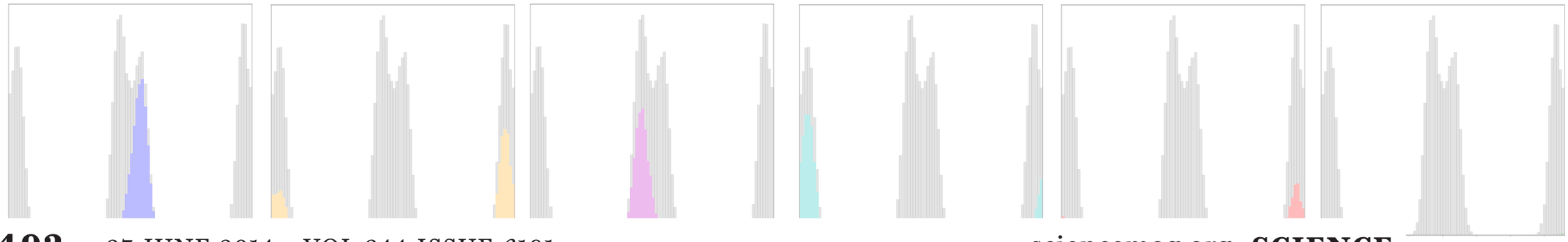












1492 27 JUNE 2014 • VOL 344 ISSUE 6191 sciencemag.org SCIENCE

MACHINE LEARNING

Clustering by fast search and find of density peaks

Alex Rodriguez and Alessandro Laio

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent:

$$m\ddot{\mathbf{R}} = -\frac{\partial E}{\partial \mathbf{R}}$$

$$p_c = \frac{T_c}{T}$$

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent;

2. for each of the most populated molecular conformers thus identified, run a 10-20 ps Car-Parrinello quantum MD simulation:

$$m\ddot{\mathbf{R}} = -\left\langle \psi \left| \frac{\partial \hat{H}}{\partial \mathbf{R}} \right| \psi \right\rangle$$

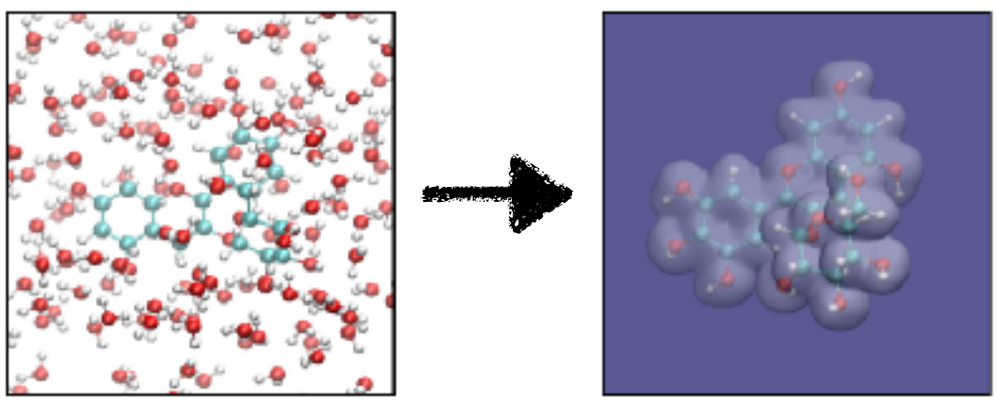
$$\mu\ddot{\psi} = -\hat{H}\psi + \Lambda\psi$$

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent;

2. for each of the most populated molecular conformers thus identified, run a 10-20 ps Car-Parrinello quantum MD simulation;

3. for each CPMD trajectory thus generated, compute TDDFpT spectra on the fly ≈ 1ps apart, treating the solvent as a dielectric continuum:



$$\mathcal{L}\tilde{\rho}'_n(t) = \omega_n(t)\tilde{\rho}'_n(t)$$

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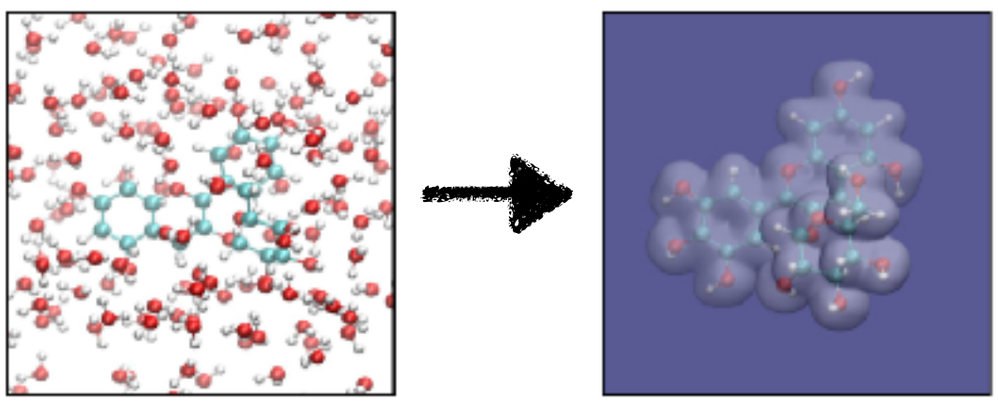

$$\mathcal{L}\tilde{\rho}'_n(t) = \omega_n(t)\tilde{\rho}'_n(t)$$

THE JOURNAL OF CHEMICAL PHYSICS **142**, 034111 (2015)

Self-consistent continuum solvation for optical absorption of complex molecular systems in solution

Iurii Timrov,[1] Oliviero Andreussi,[2] Alessandro Biancardi,[1] Nicola Marzari,[3] and Stefano Baroni[1,3,a)]

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent;

2. for each of the most populated molecular conformers thus identified, run a 10-20 ps Car-Parrinello quantum MD simulation;

3. for each CPMD trajectory thus generated, compute TDDFpT spectra on the fly ≈ 1ps apart, treating the solvent as a dielectric continuum:

4. average the spectra within each conformer and over different conformers:

$$S_c(\omega) = \left\langle \sum_n f_n(t)\delta\big(\omega - \omega_n(t)\big) \right\rangle_c$$

$$S(\omega) = \sum_c p_c S_c(\omega)$$

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent;

2. for each of the most populated molecular conformers thus identified, run a 10-20 ps Car-Parrinello quantum MD simulation;

3. for each CPMD trajectory thus generated, compute TDDFpT spectra on the fly ≈ 1ps apart, treating the solvent as a dielectric continuum:

4. average the spectra within each conformer and over different conformers:

JCTC Journal of Chemical Theory and Computation Article

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Multimodel Approach to the Optical Properties of Molecular Dyes in Solution

Iurii Timrov,[†,¶] Marco Micciarelli,[†] Marta Rosa,[†] Arrigo Calzolari,[‡] and Stefano Baroni*[,†]

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DOI: 10.1021/acs.jctc.6b00417
J. Chem. Theory Comput. 2016, 12, 4423−4429

the multi-scale protocol

1. estimate conformational populations from long (> 1μs) classical MD simulations in explicit water solvent;

2. for each of the most populated molecular conformers thus identified, run a 10-20 ps Car-Parrinello quantum MD simulation;

3. for each CPMD trajectory thus generated, compute TDDFpT spectra on the fly (1ps long part, treating the solvent as a dielectric continuum;

4. average the spectra within each conformer and over different conformers:

QUANTUMESPRESSO

JCTC Journal of Chemical Theory and Computation — Article

pubs.acs.org/JCTC

Multimodel Approach to the Optical Properties of Molecular Dyes in Solution

Iurii Timrov,[†,¶] Marco Micciarelli,[†] Marta Rosa,[†] Arrigo Calzolari,[‡] and Stefano Baroni*[,†]

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DOI: 10.1021/acs.jctc.6b00417
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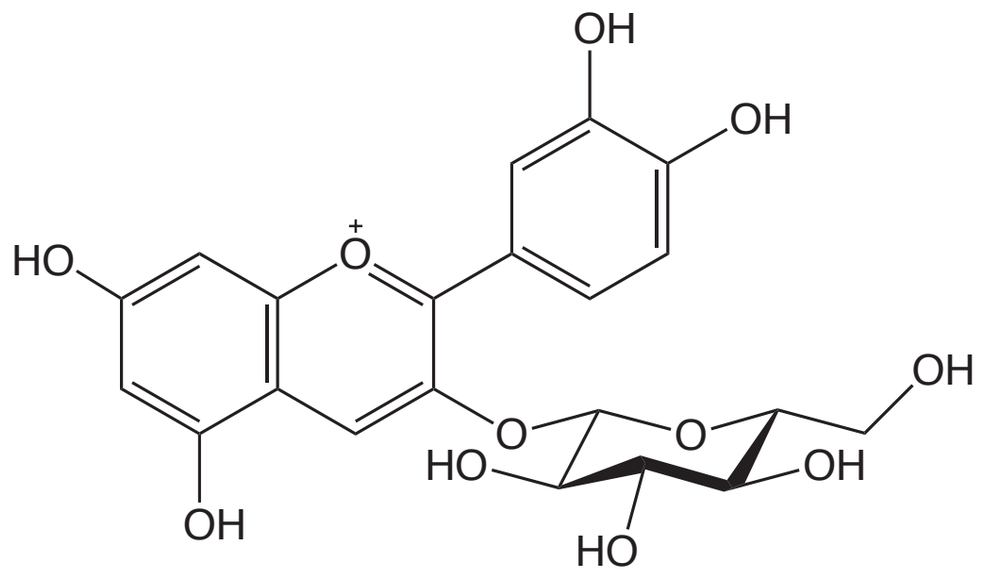
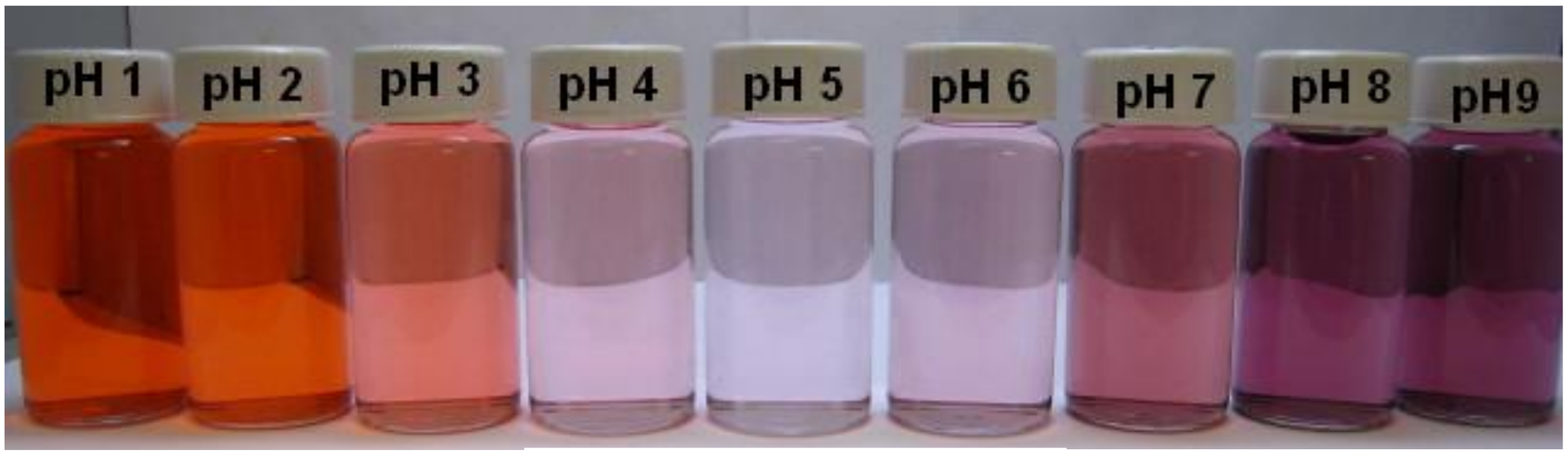
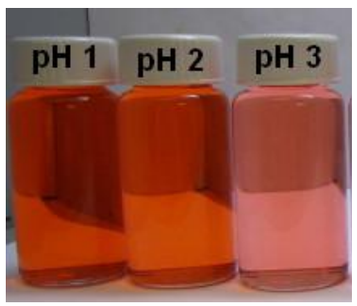
effects of the environment: acidity



Cyanidin 3-O-glucoside



effects of the environment: acidity



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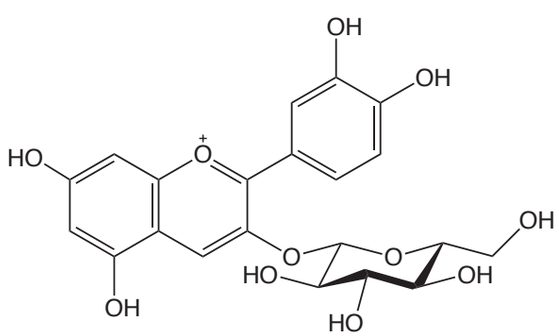
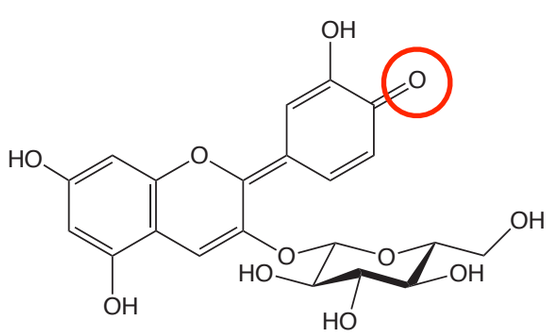


AH+ flavylium cation

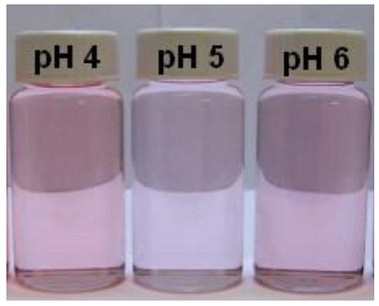
-H+

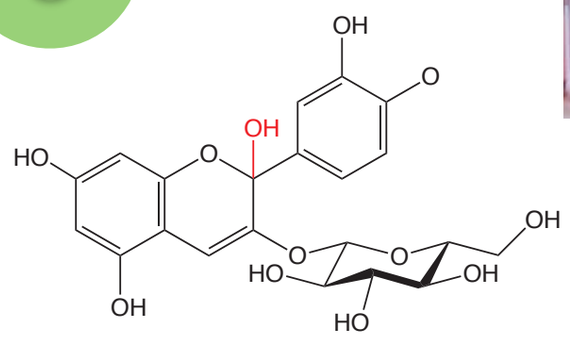


A - quinoidal base

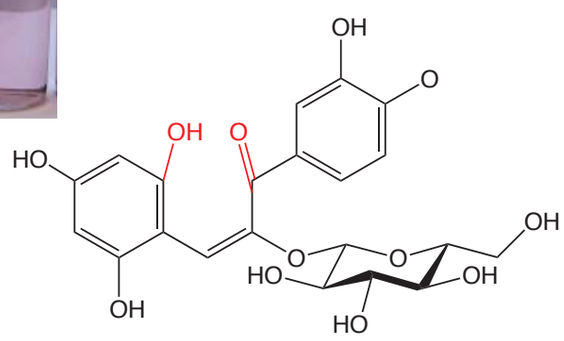
0

+OH-

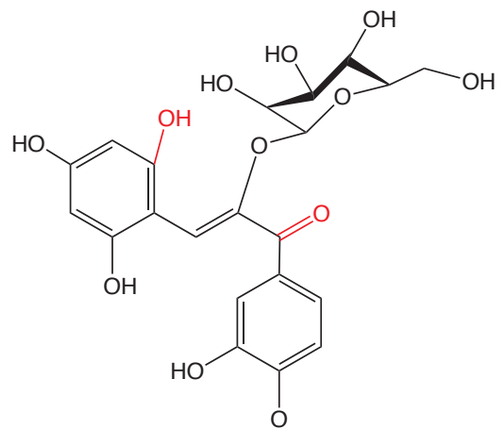




B - carbinol

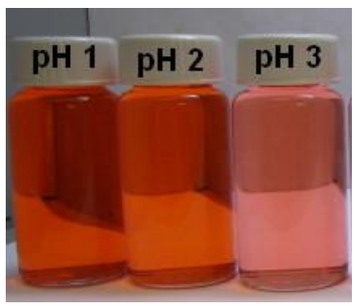


Cc - cis-chalcone



Ct - trans-chalcone

effects of the environment: acidity



+

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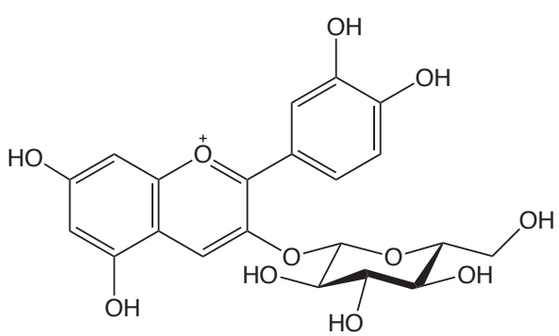

AH+ flavylium cation

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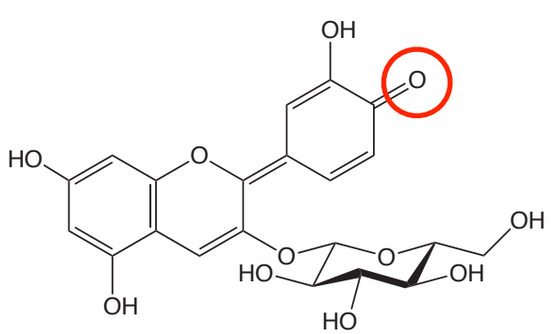
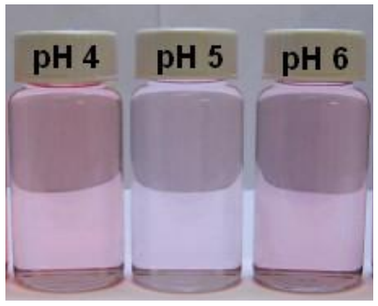
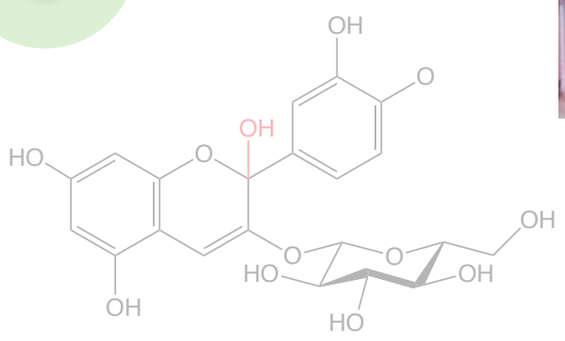


A - quinoidal base

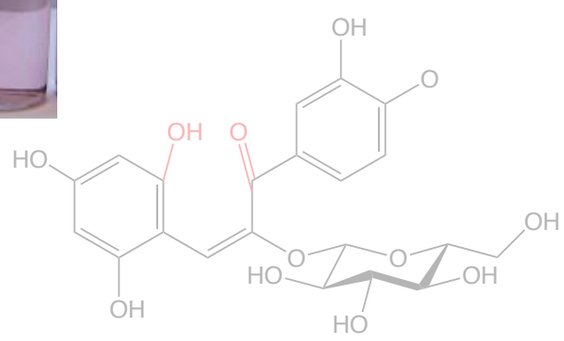
+OH-

0

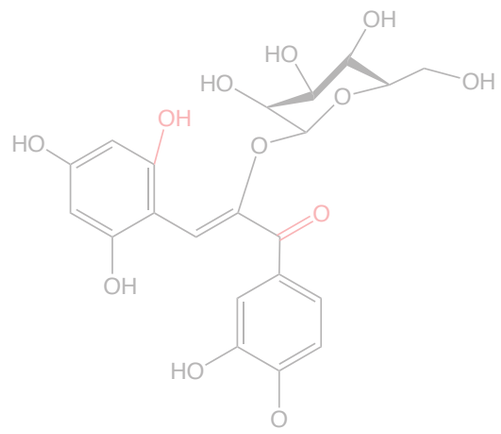




B - carbinol

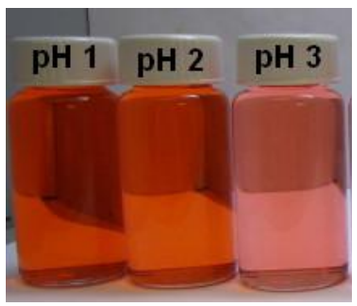


Cc - cis-chalcone



Ct - trans-chalcone

effects of the environment: acidity



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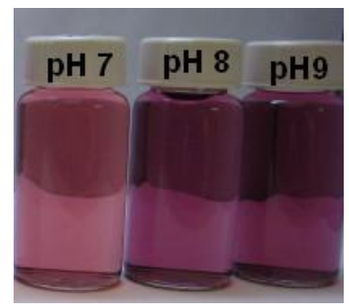

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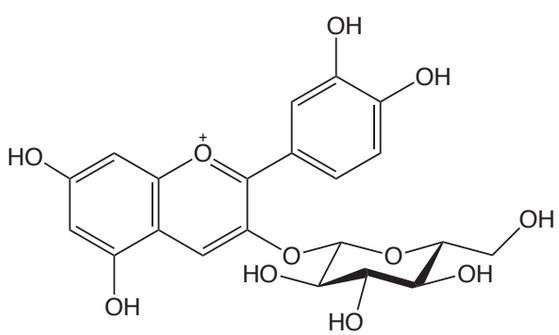

AH+ flavylium cation

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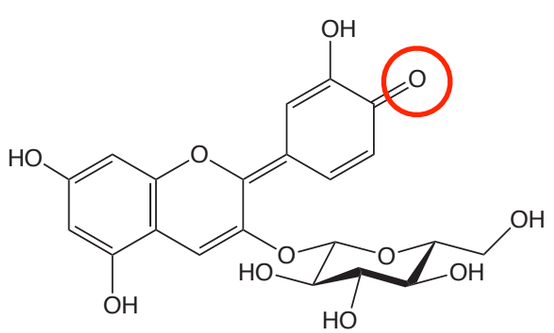

A - quinoidal base

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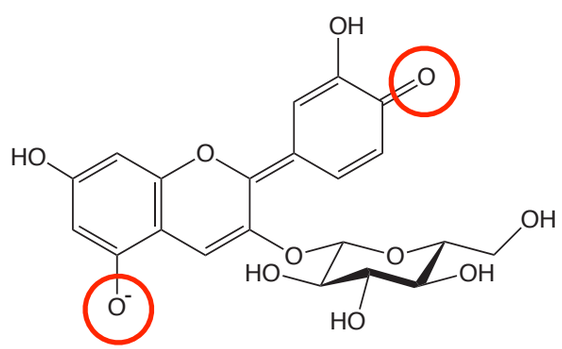

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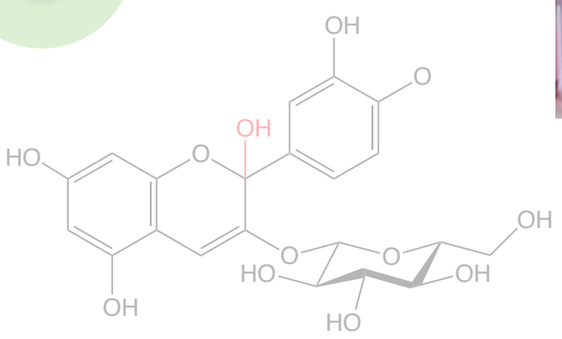
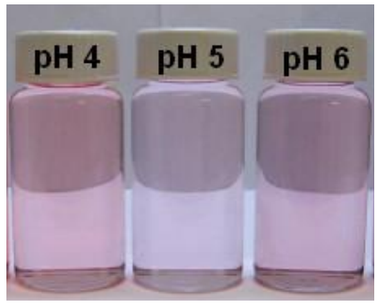
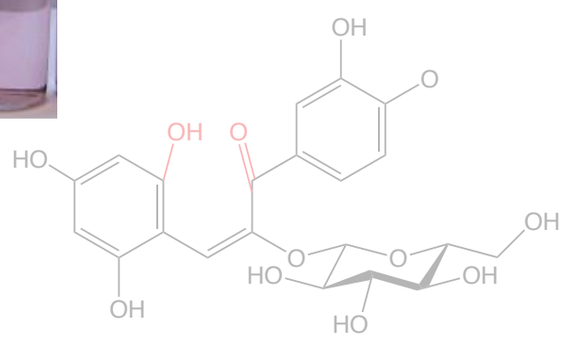
+OH-



B - carbinol





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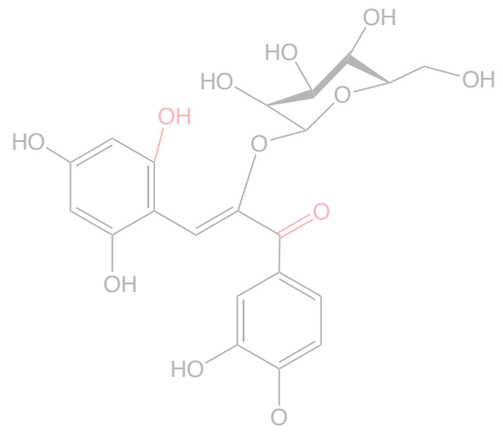

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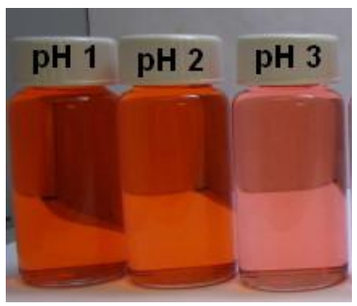
effects of the environment: acidity



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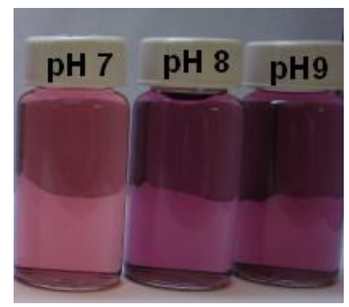

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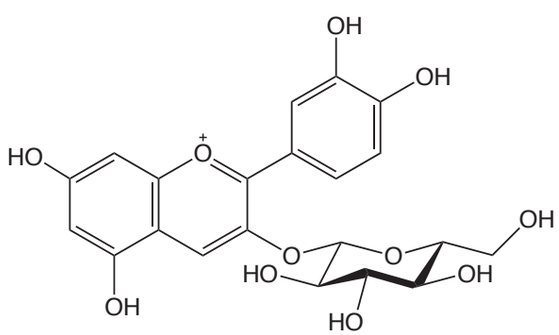
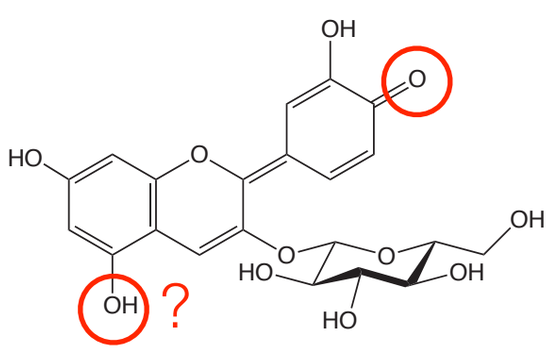


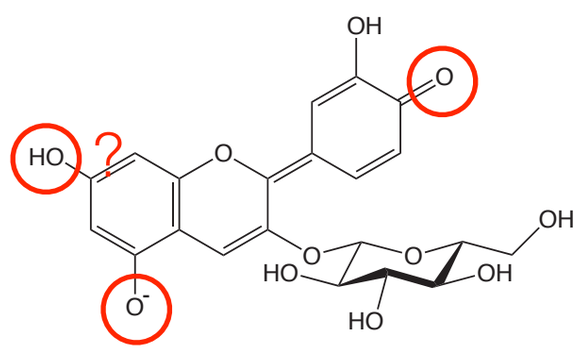
AH+ flavylium cation

-H+



A - quinoidal base

-H+



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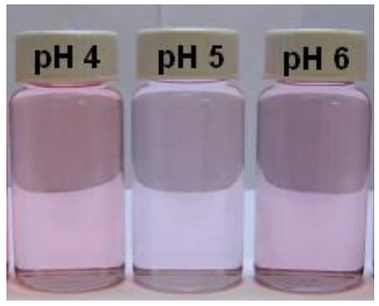
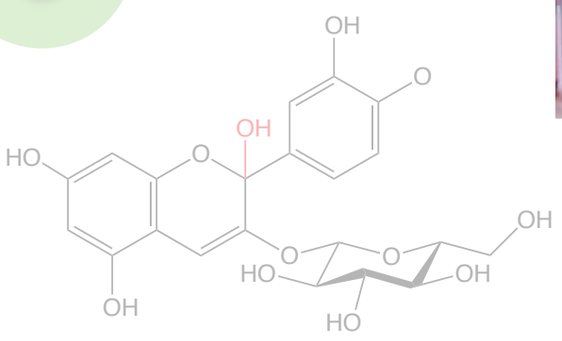
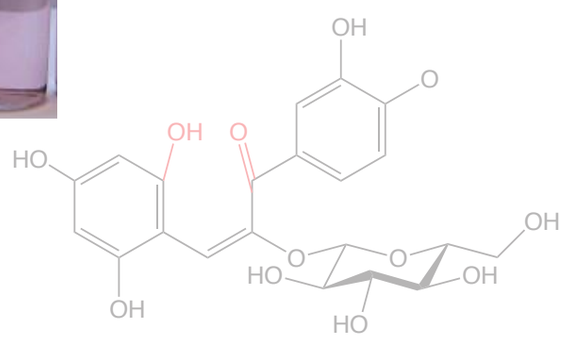
+OH-

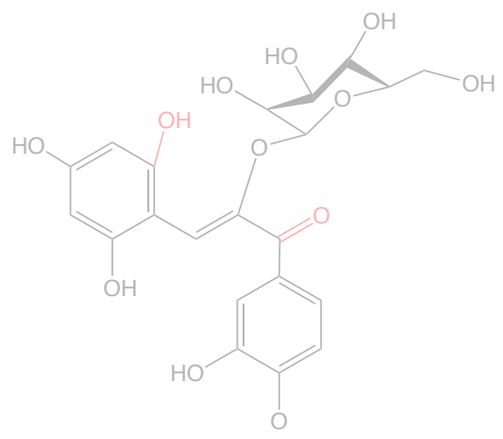




B - carbinol

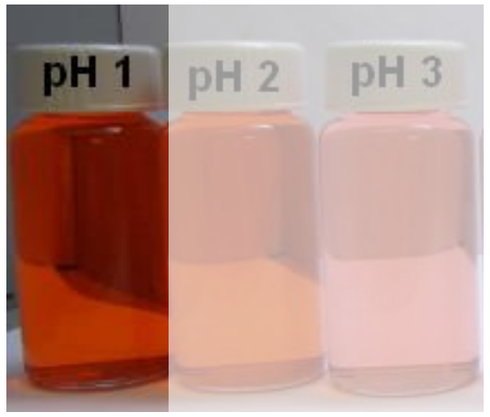


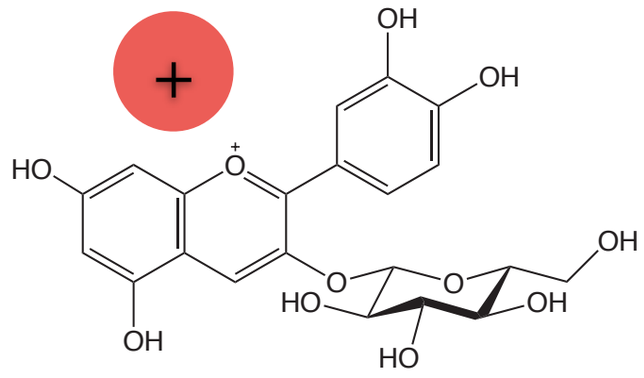
Cc - cis-chalcone



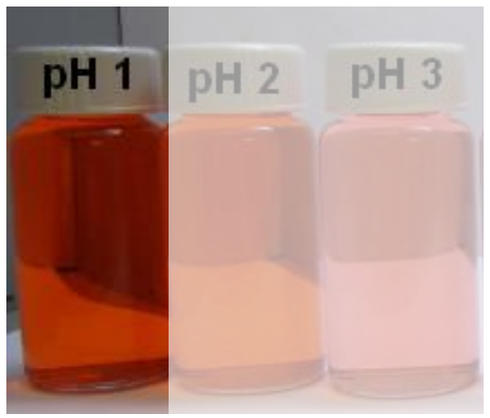
Ct - trans-chalcone

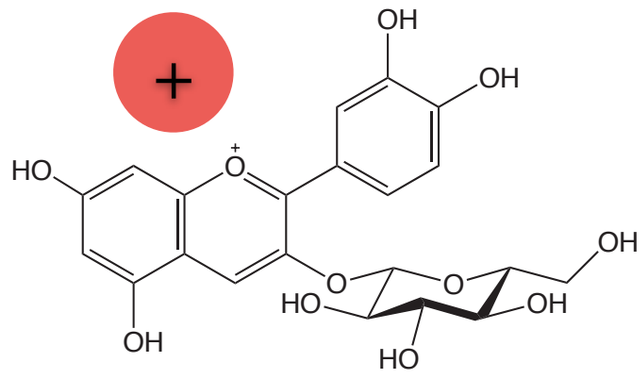
comparing predictions with experiments

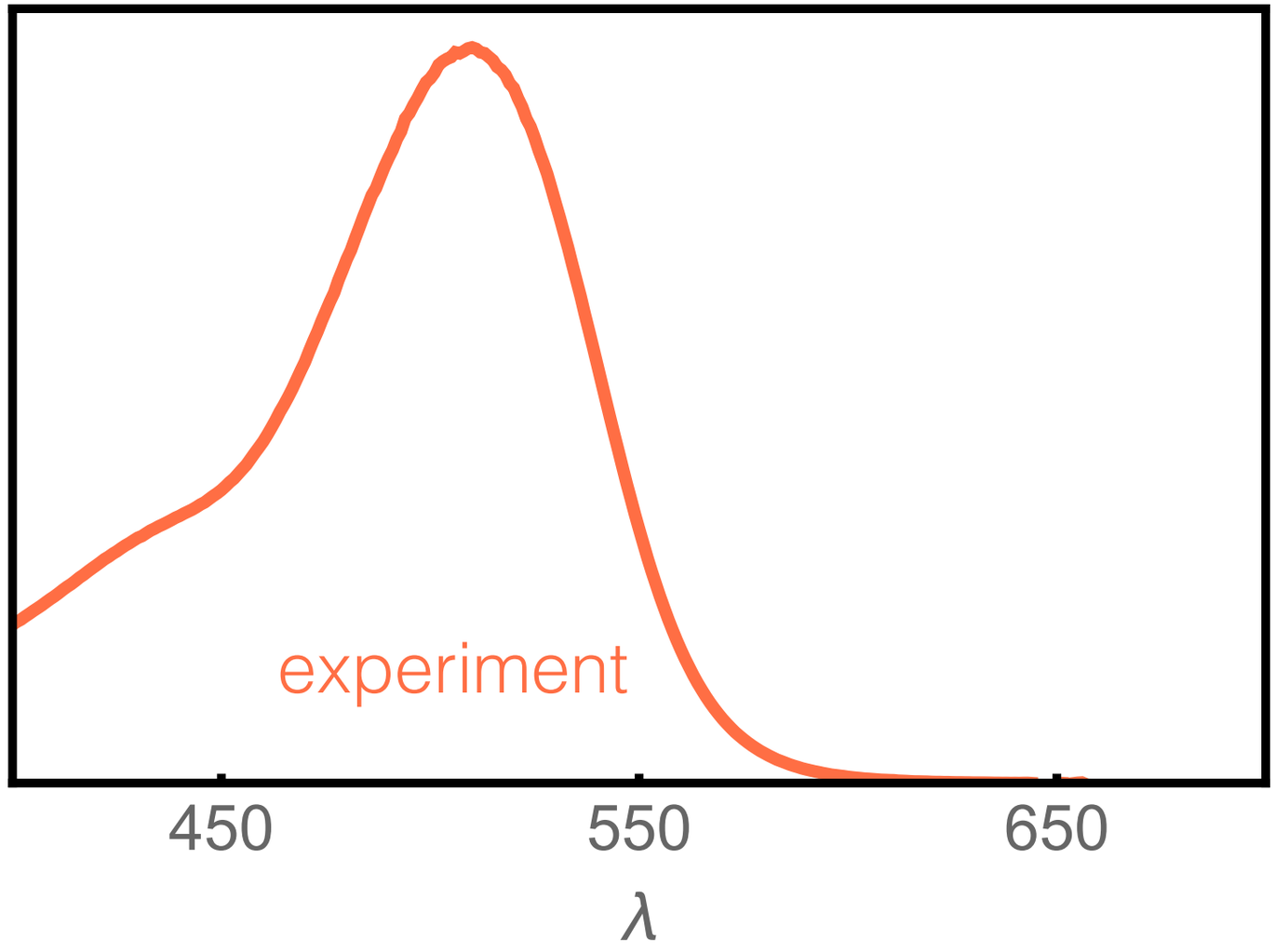




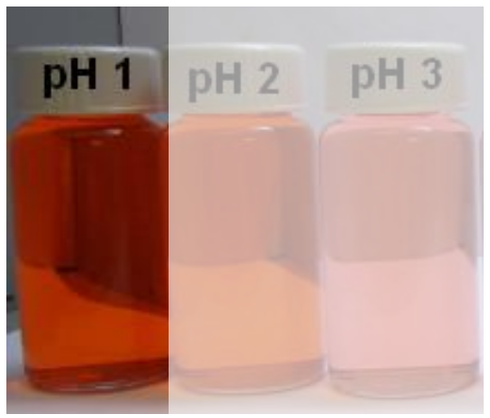
comparing predictions with experiments

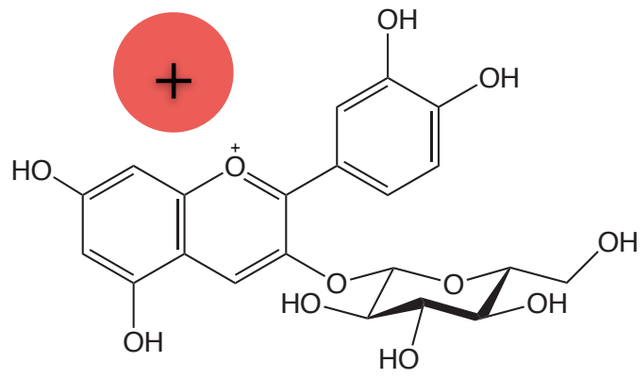


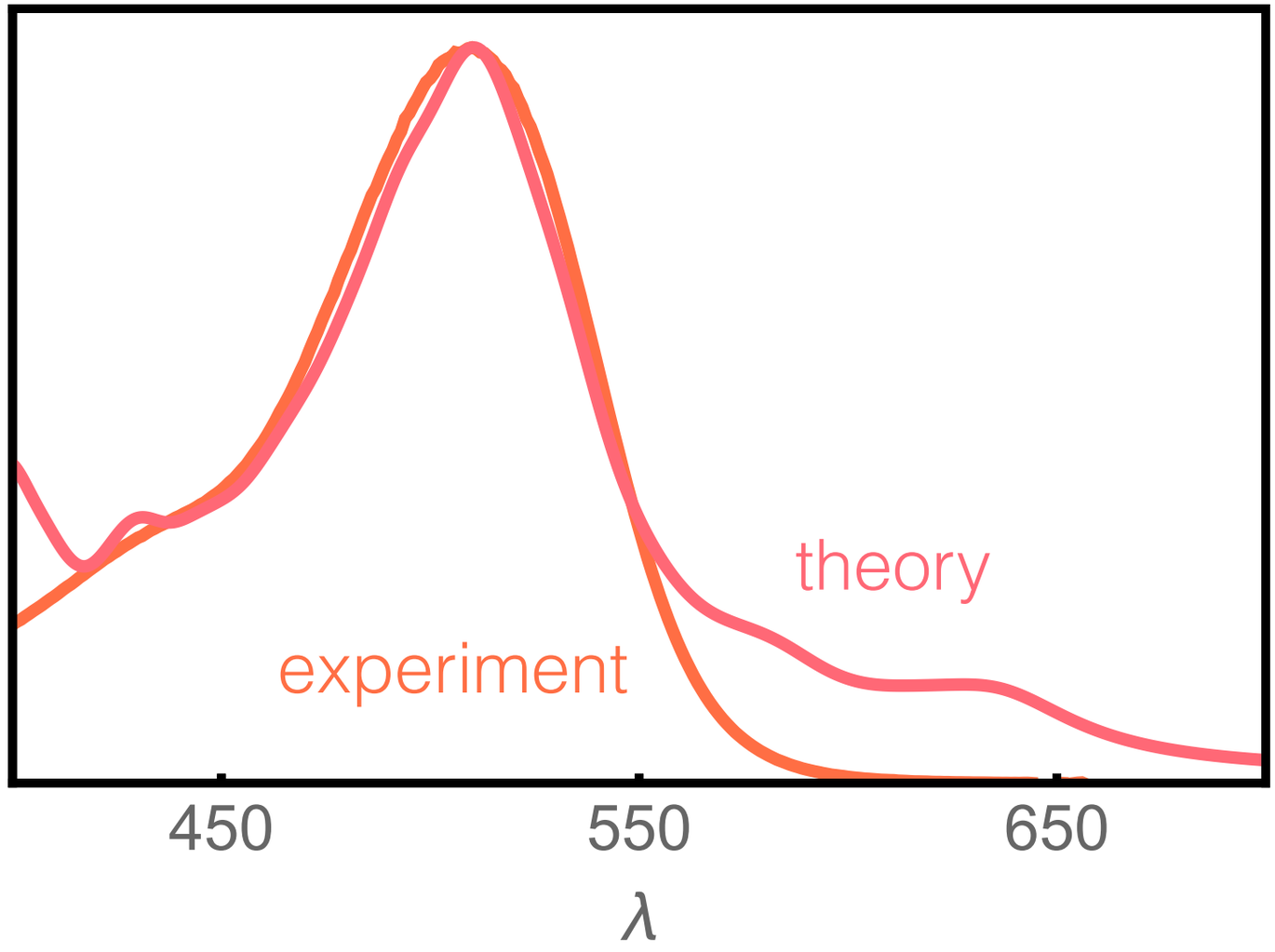




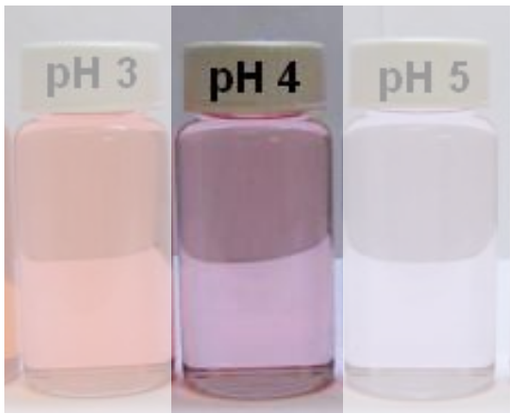
comparing predictions with experiments

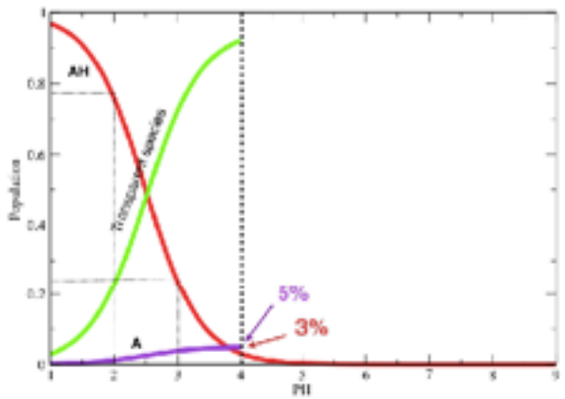


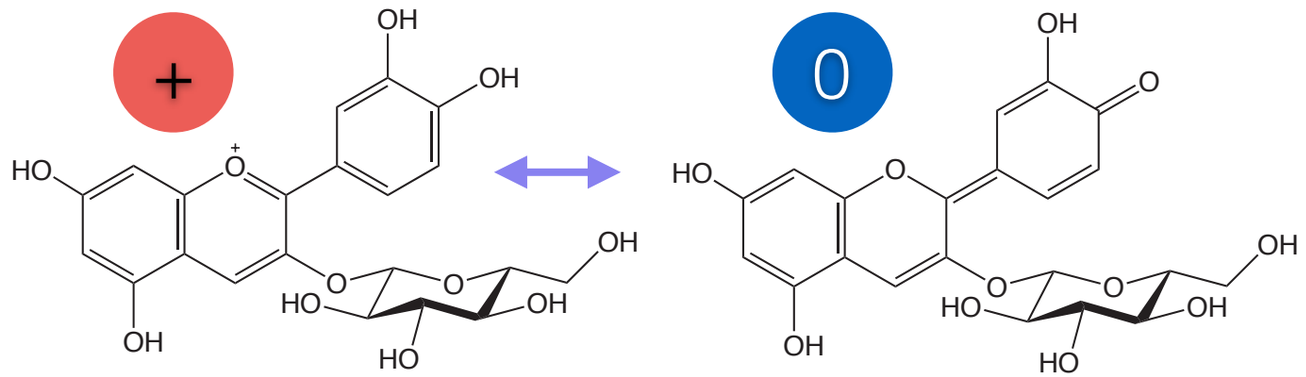


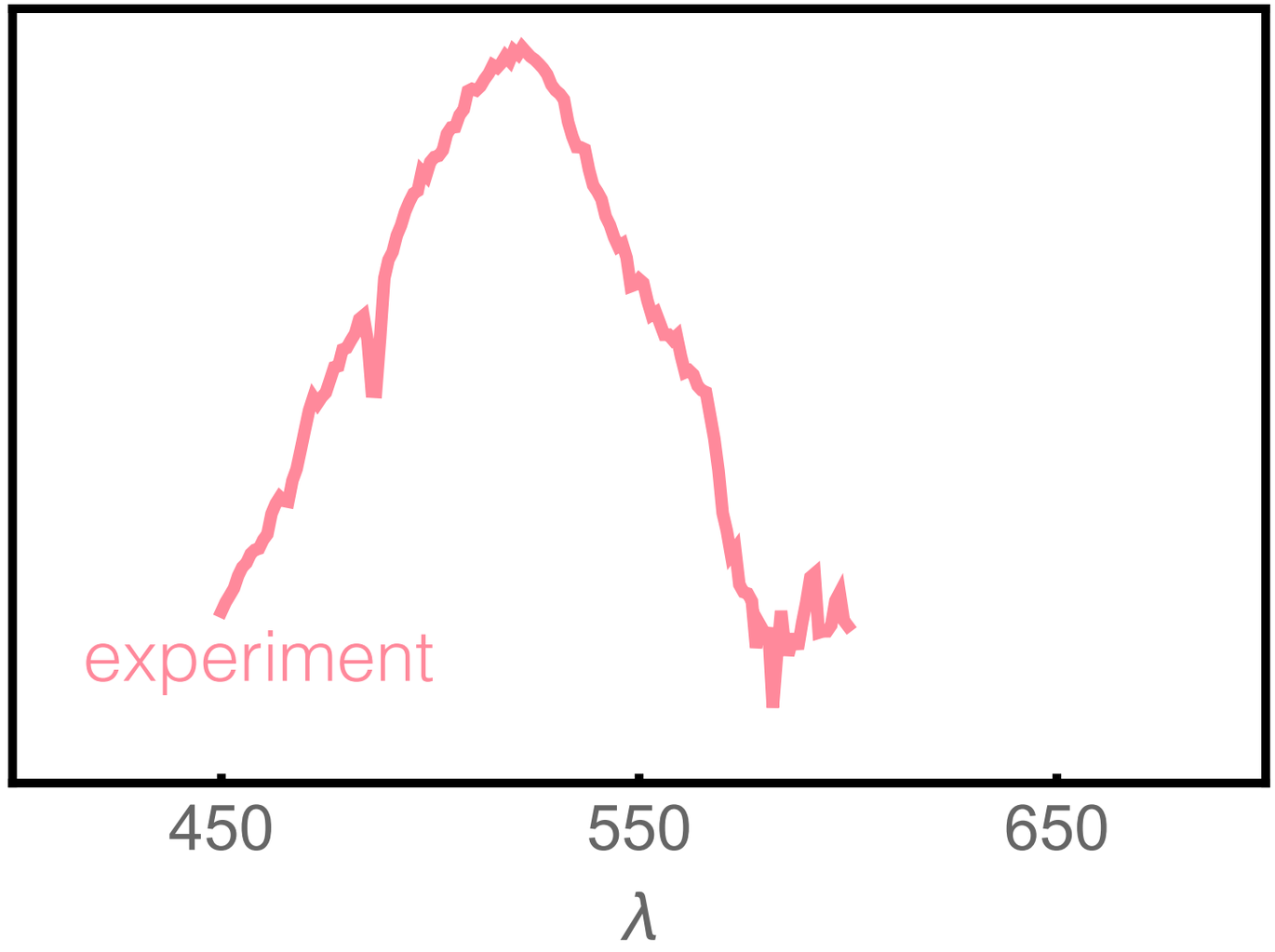


comparing predictions with experiments

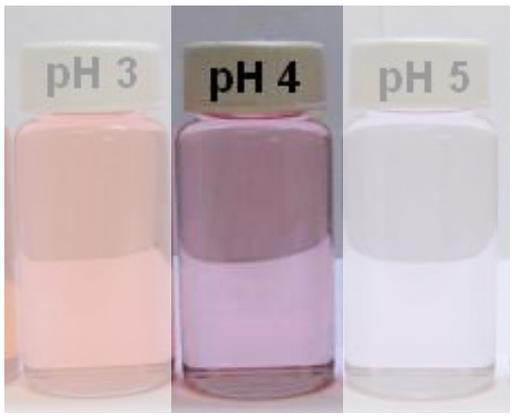


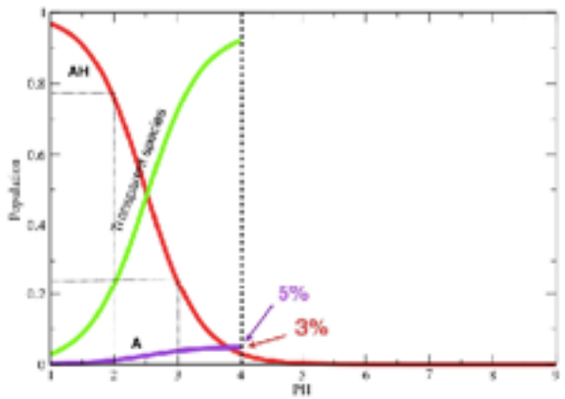


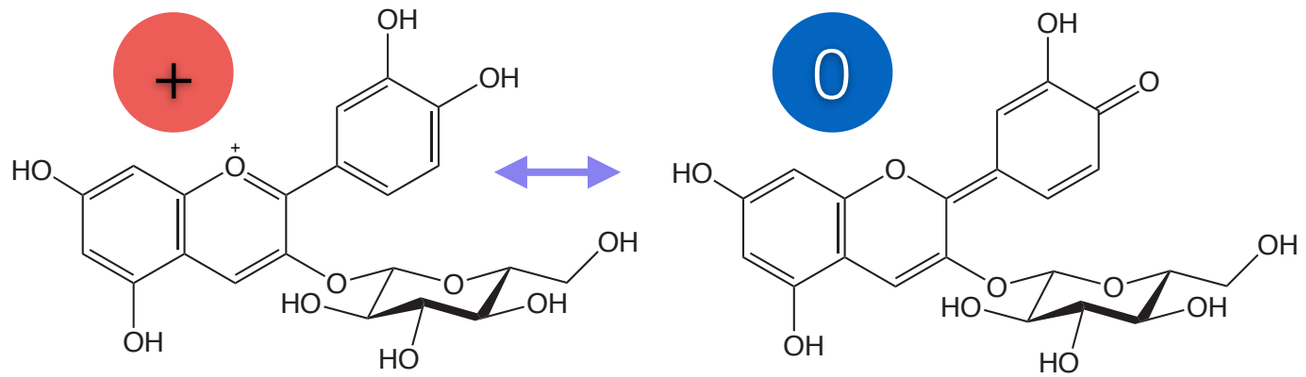


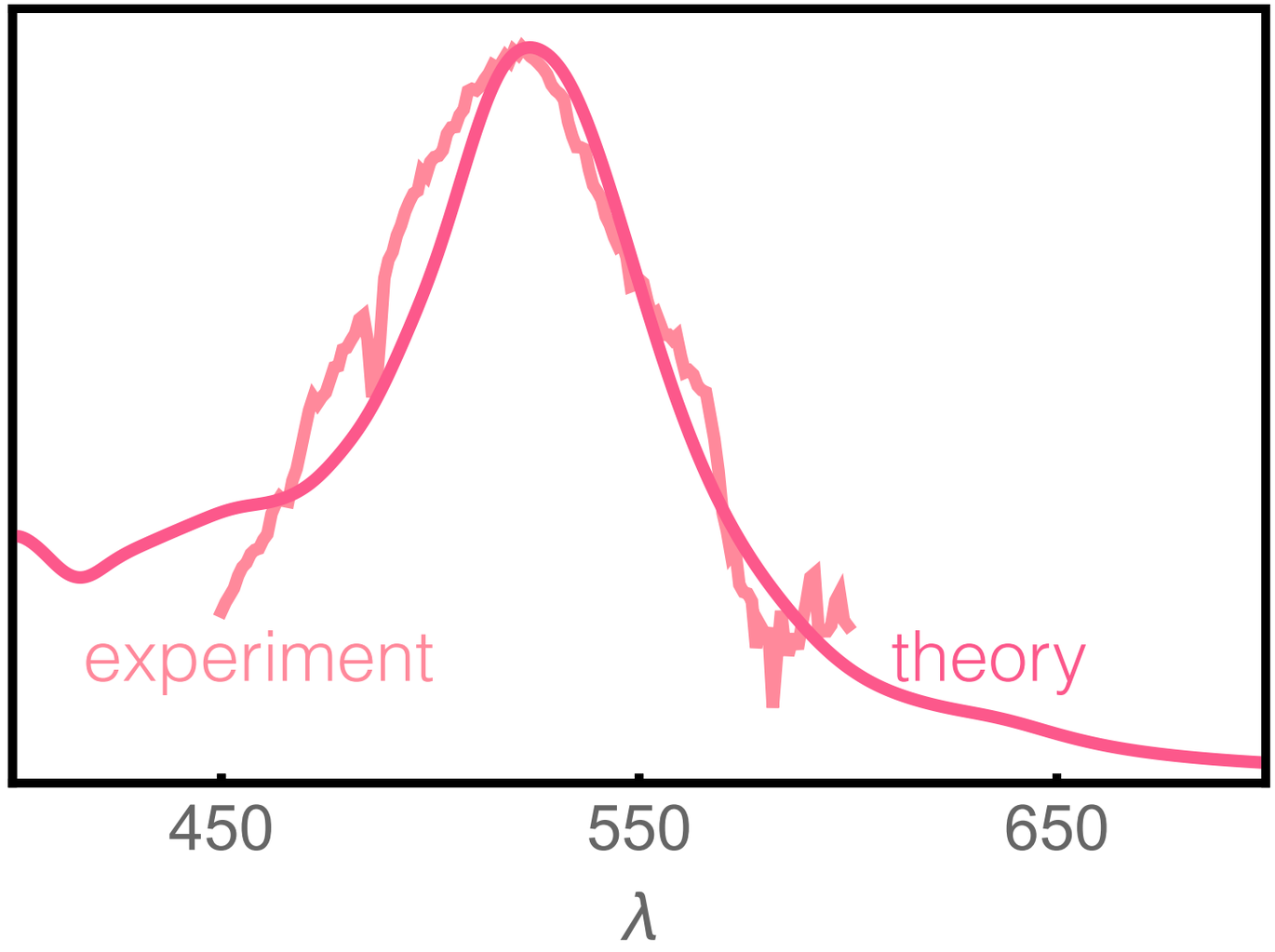


comparing predictions with experiments

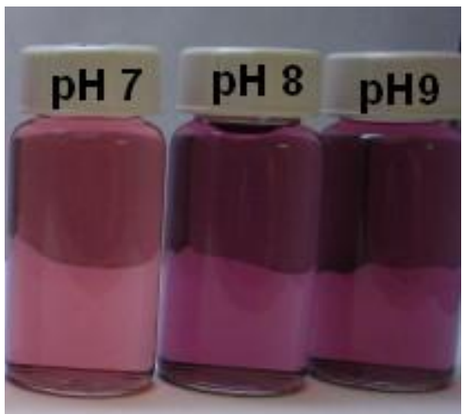


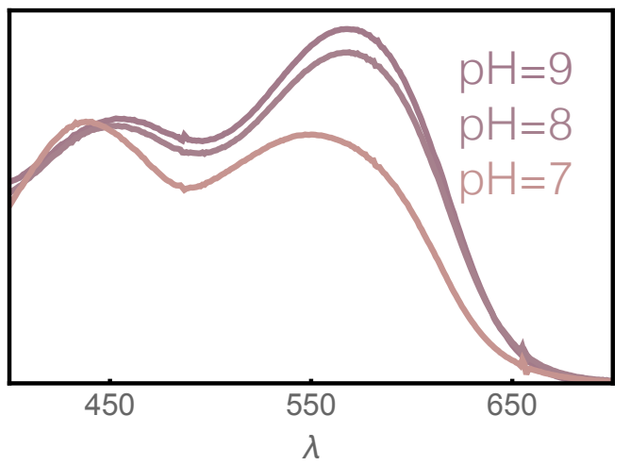


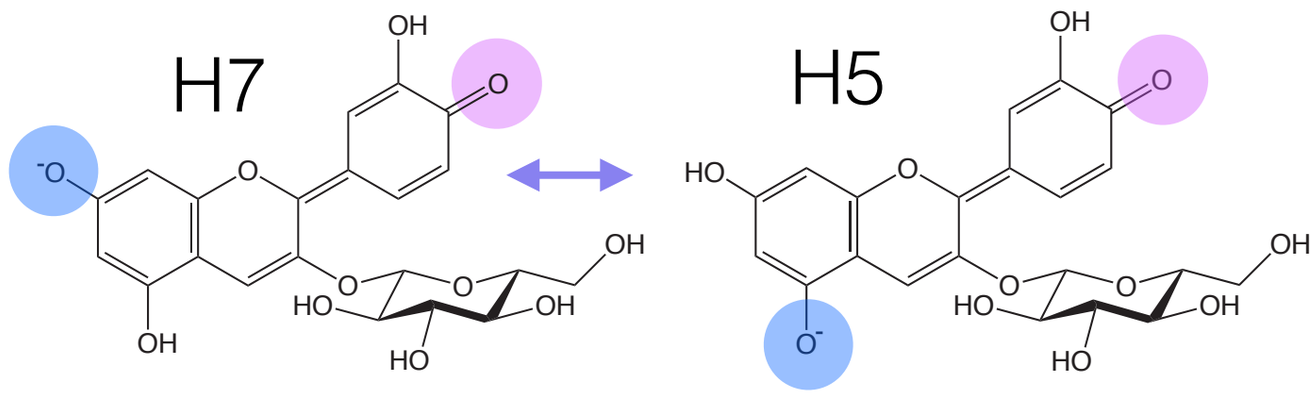


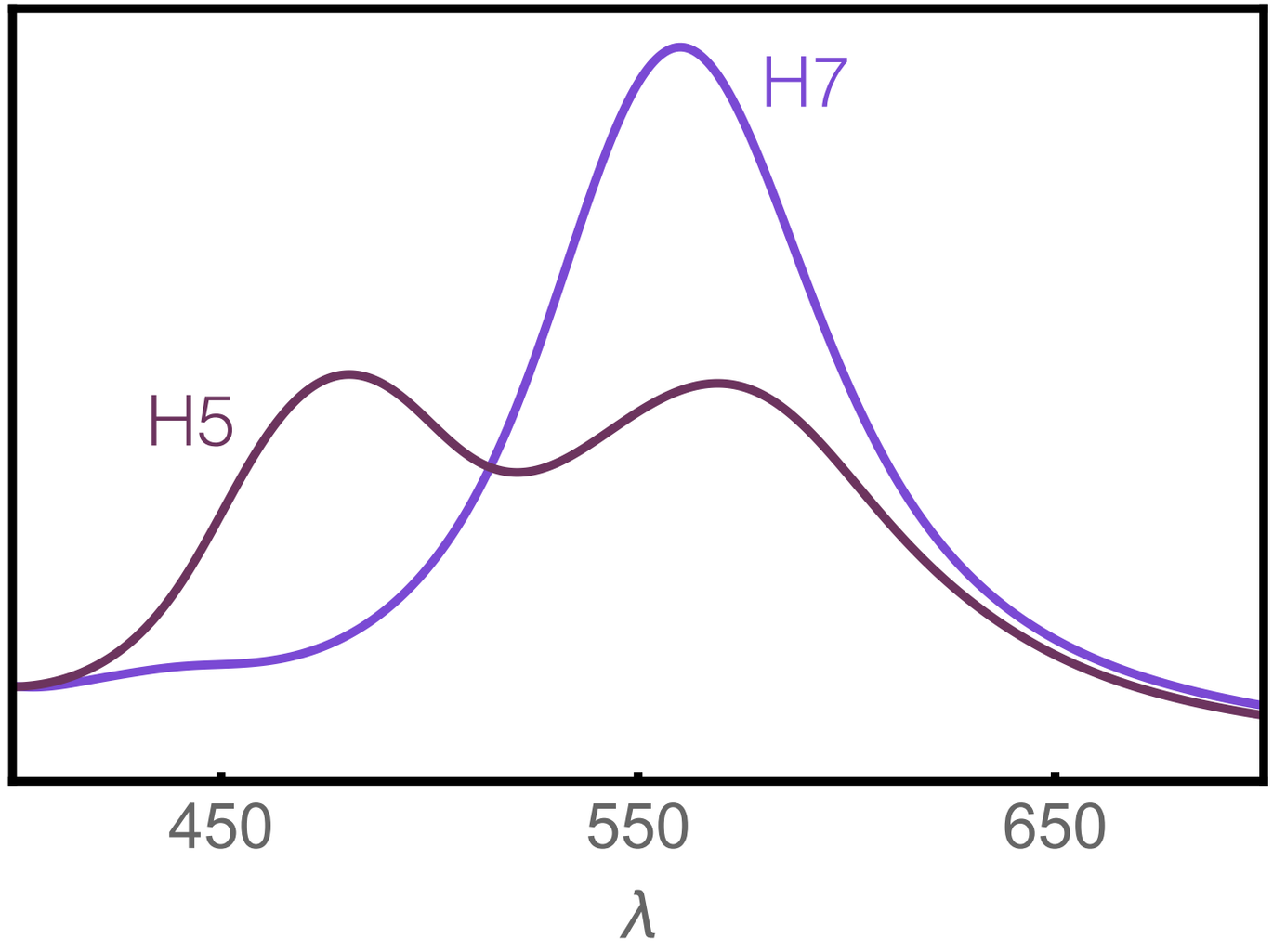


comparing predictions with experiments

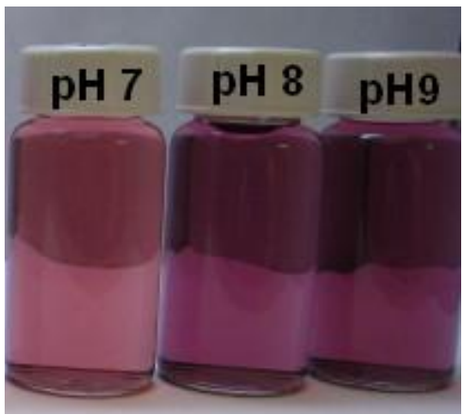


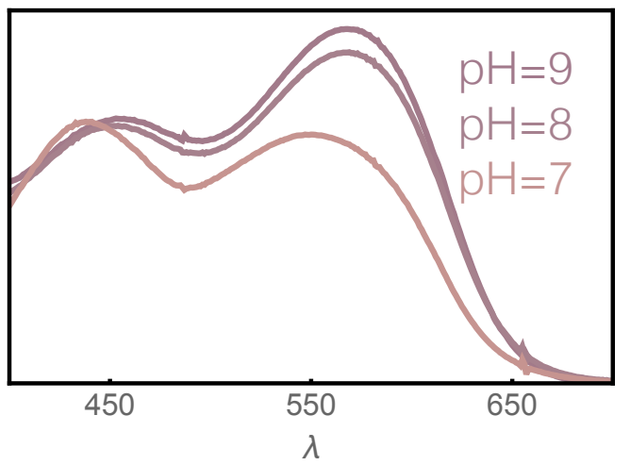


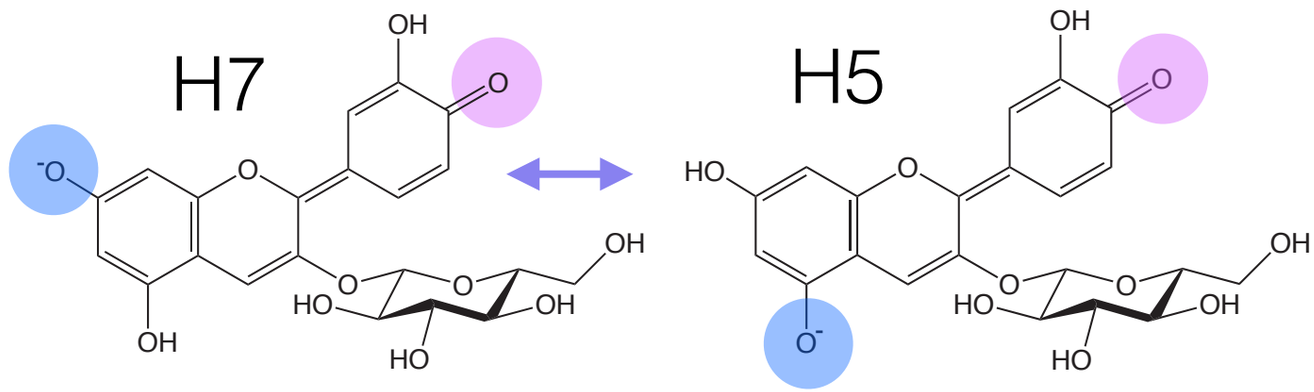




comparing predictions with experiments







comparing predictions with experiments

Check for updates

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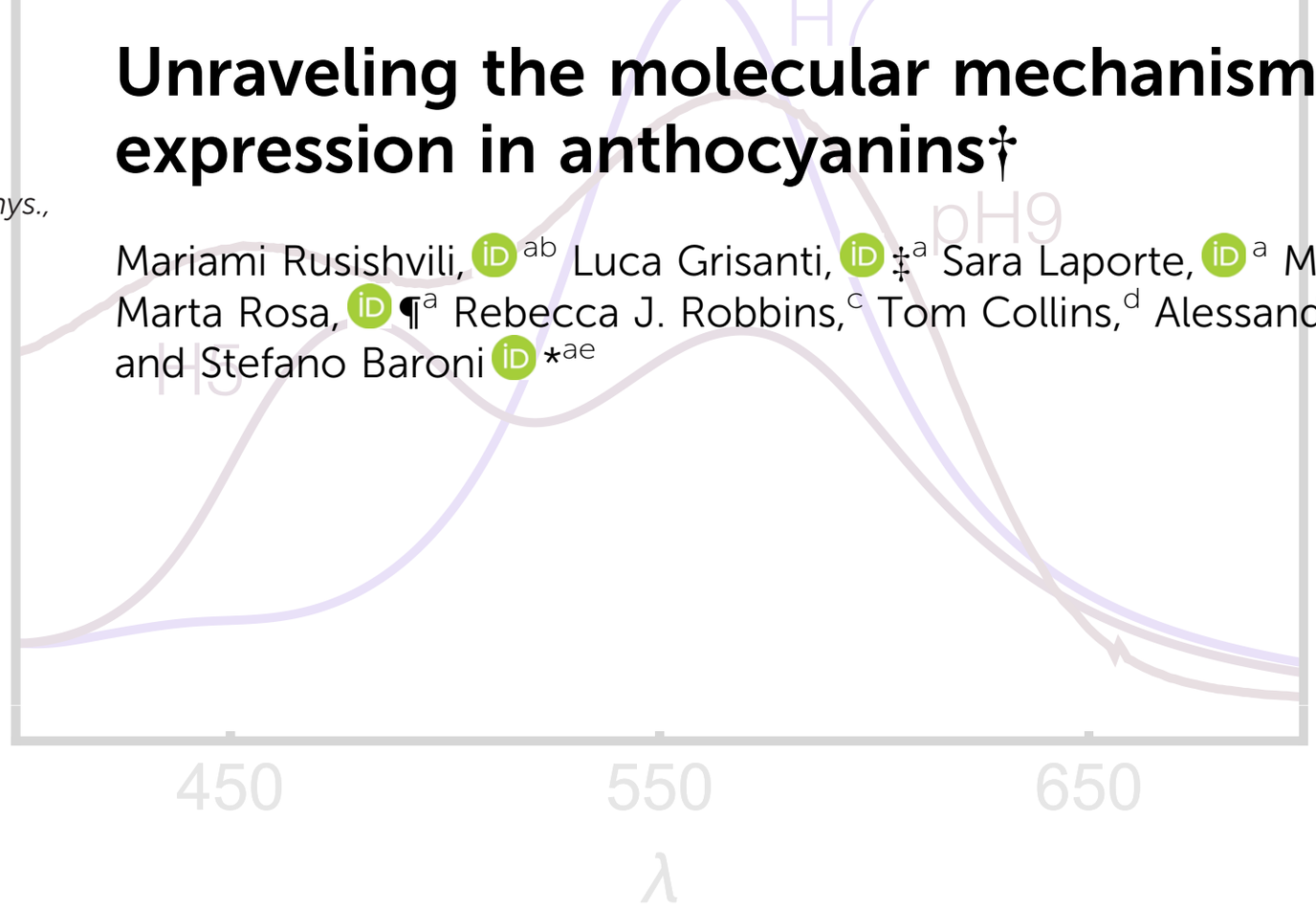
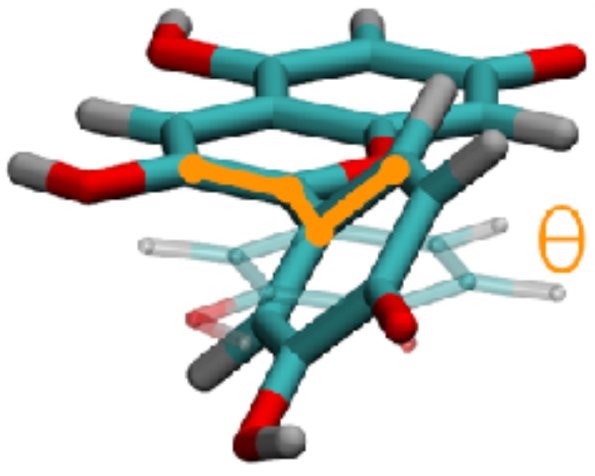
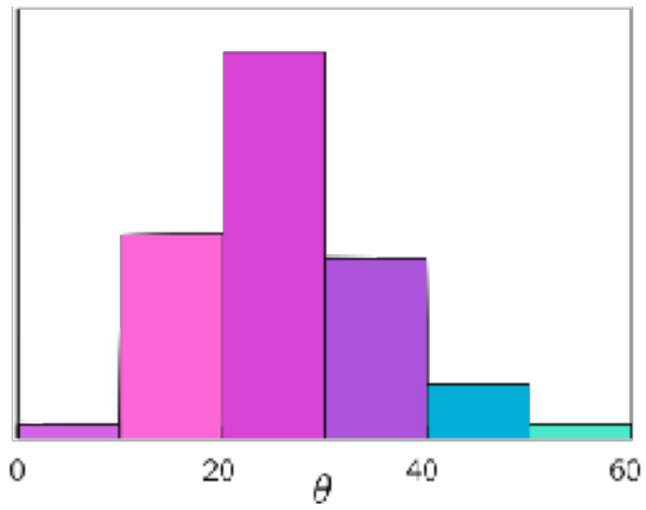
Unraveling the molecular mechanisms of color expression in anthocyanins†

Mariami Rusishvili, [ab] Luca Grisanti, [‡a] Sara Laporte, [a] Marco Micciarelli, [§a] Marta Rosa, [¶a] Rebecca J. Robbins,[c] Tom Collins,[d] Alessandra Magistrato [e] and Stefano Baroni [*ae]



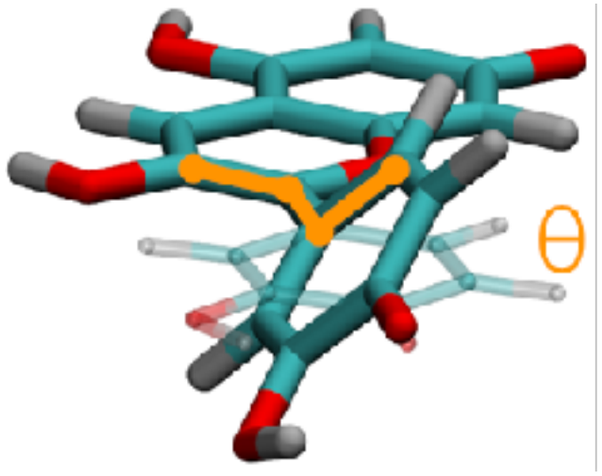
in the quest for a natural *blue 1*

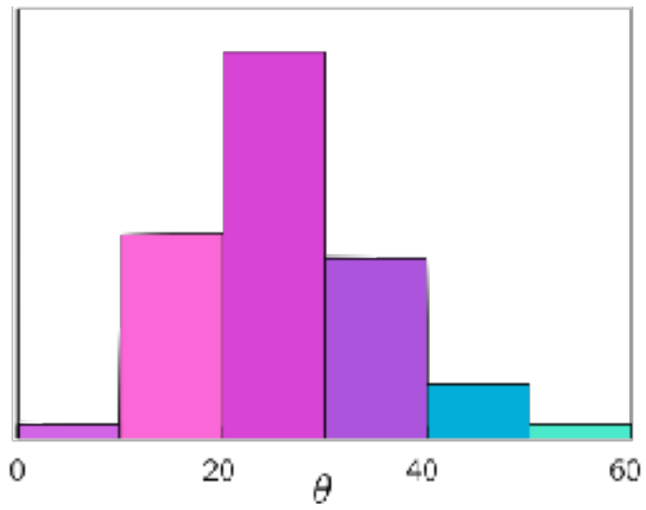


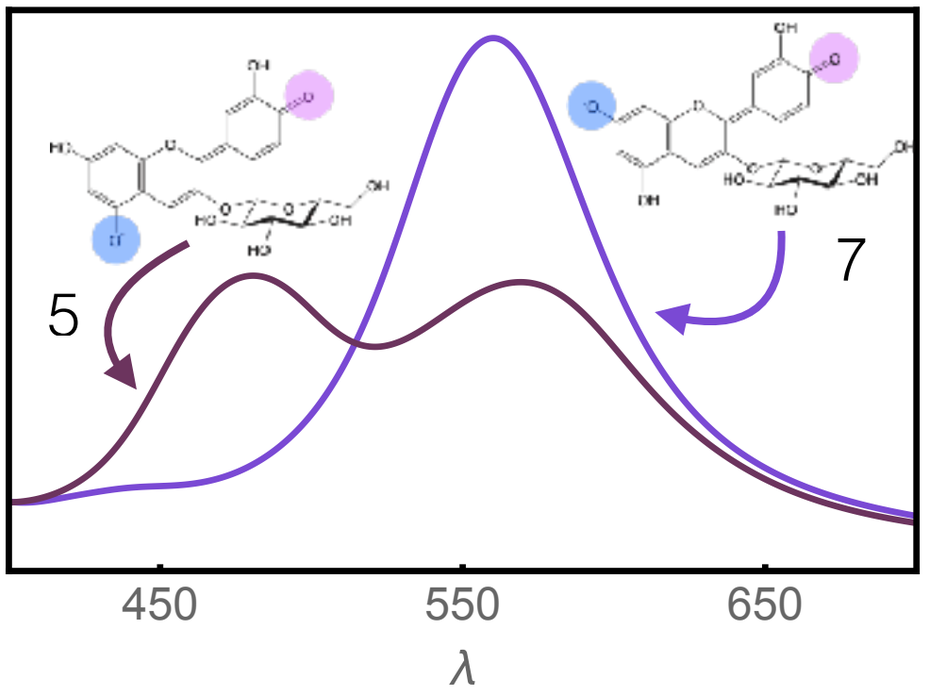


1. bend the CB bond

in the quest for a natural *blue 1*

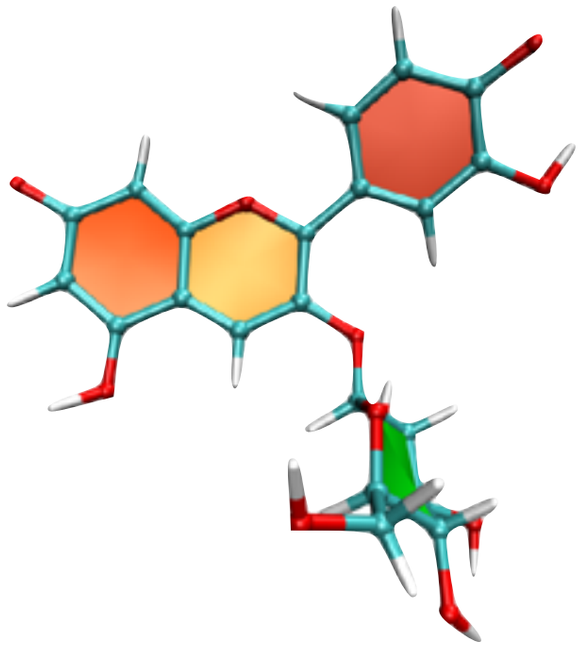


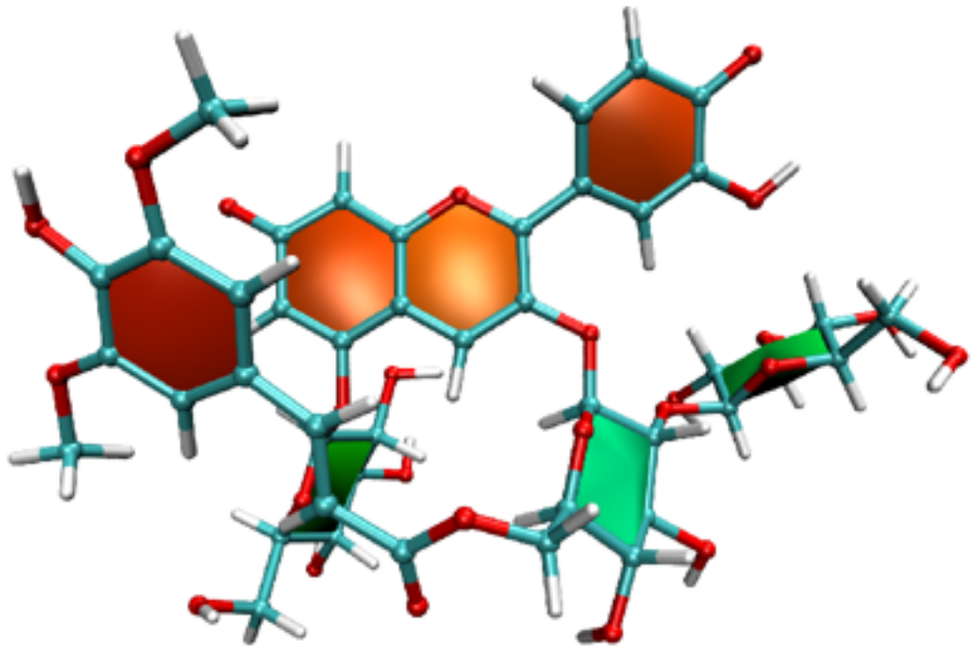


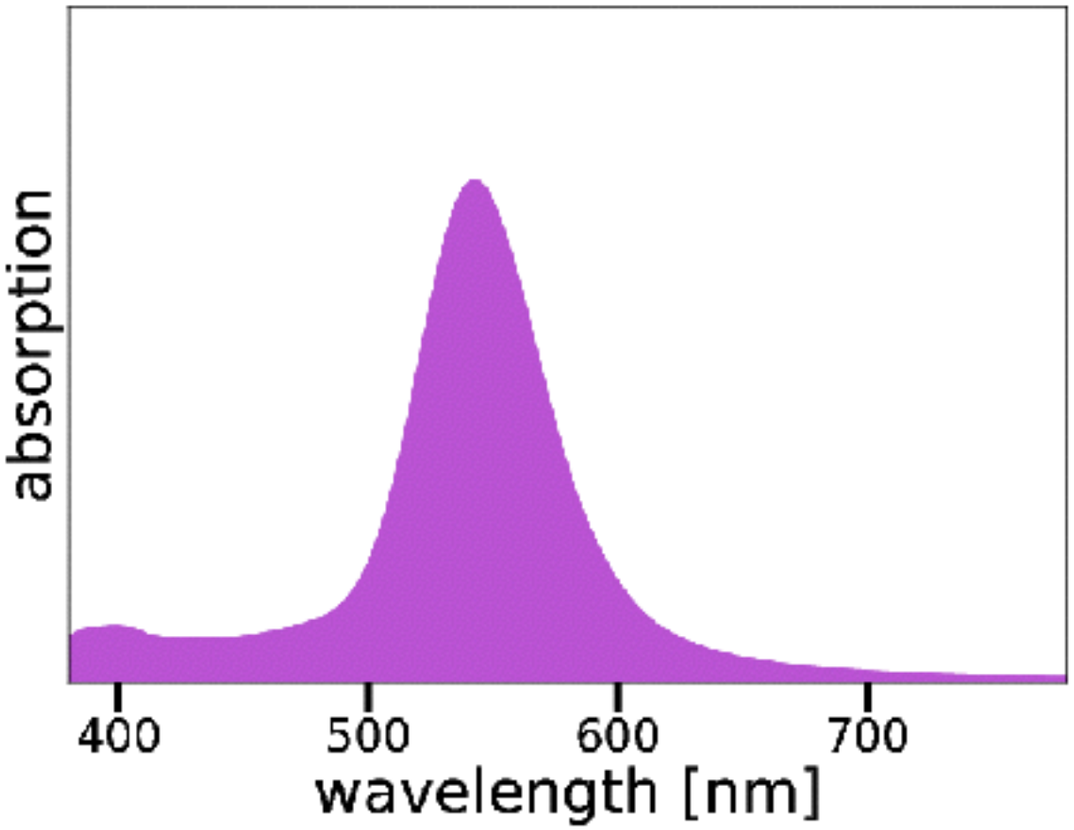


1. bend the CB bond
2. inhibit deprotonation at 5

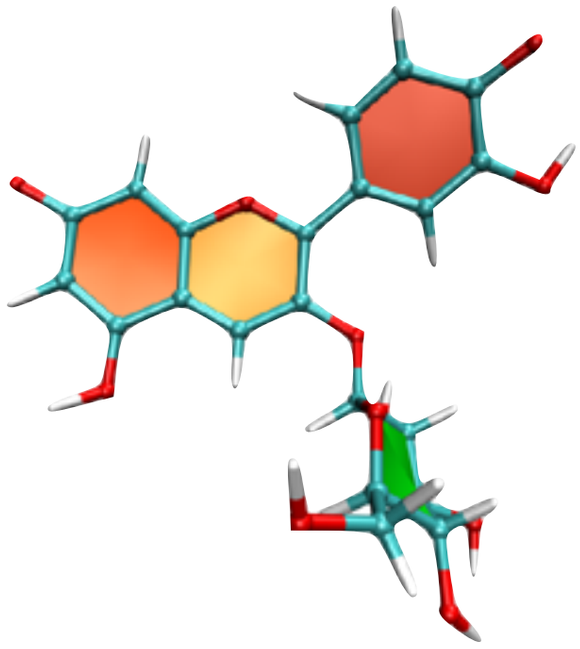
in the quest for a natural *blue 1*

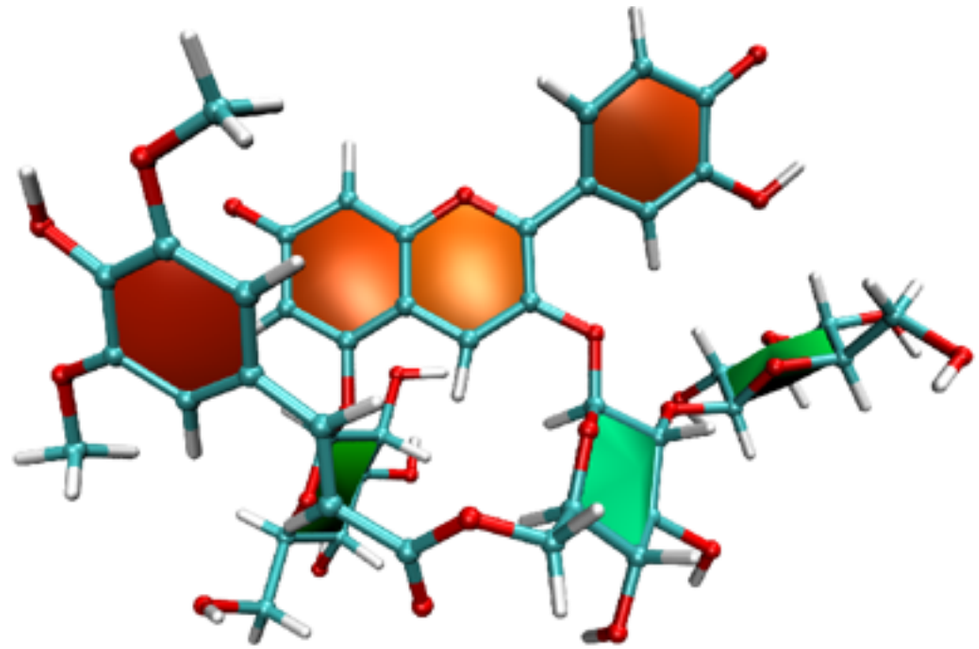


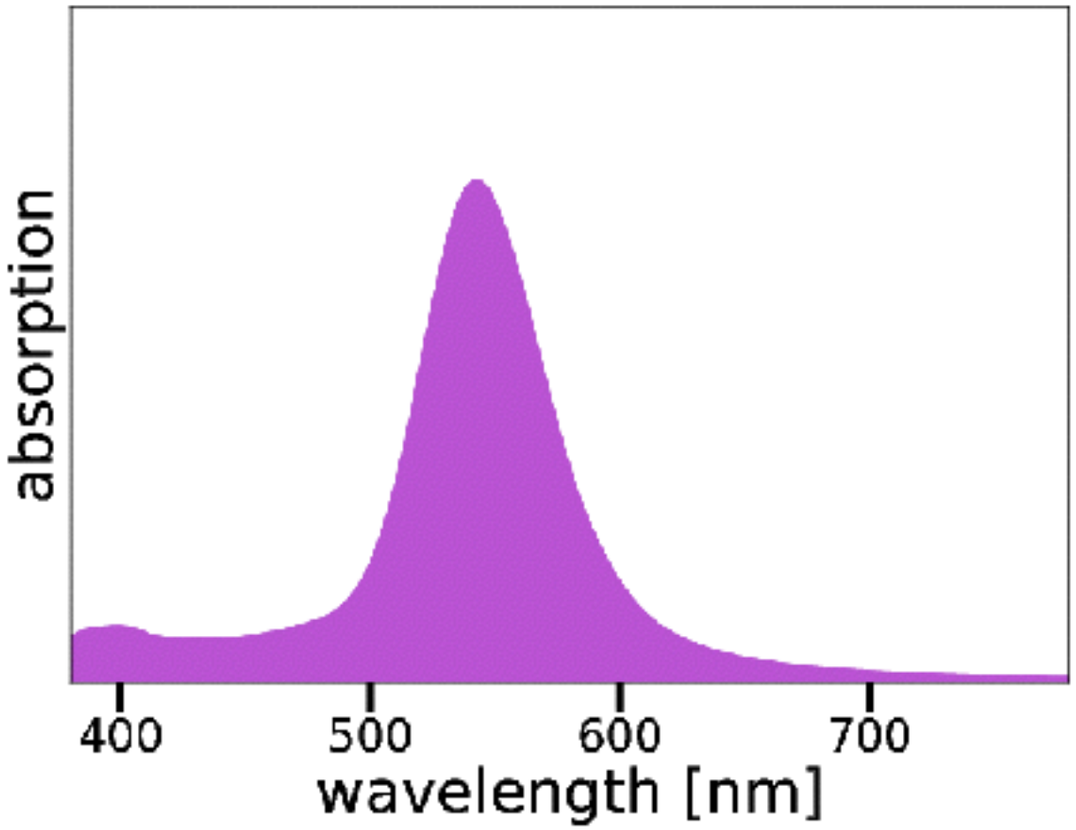


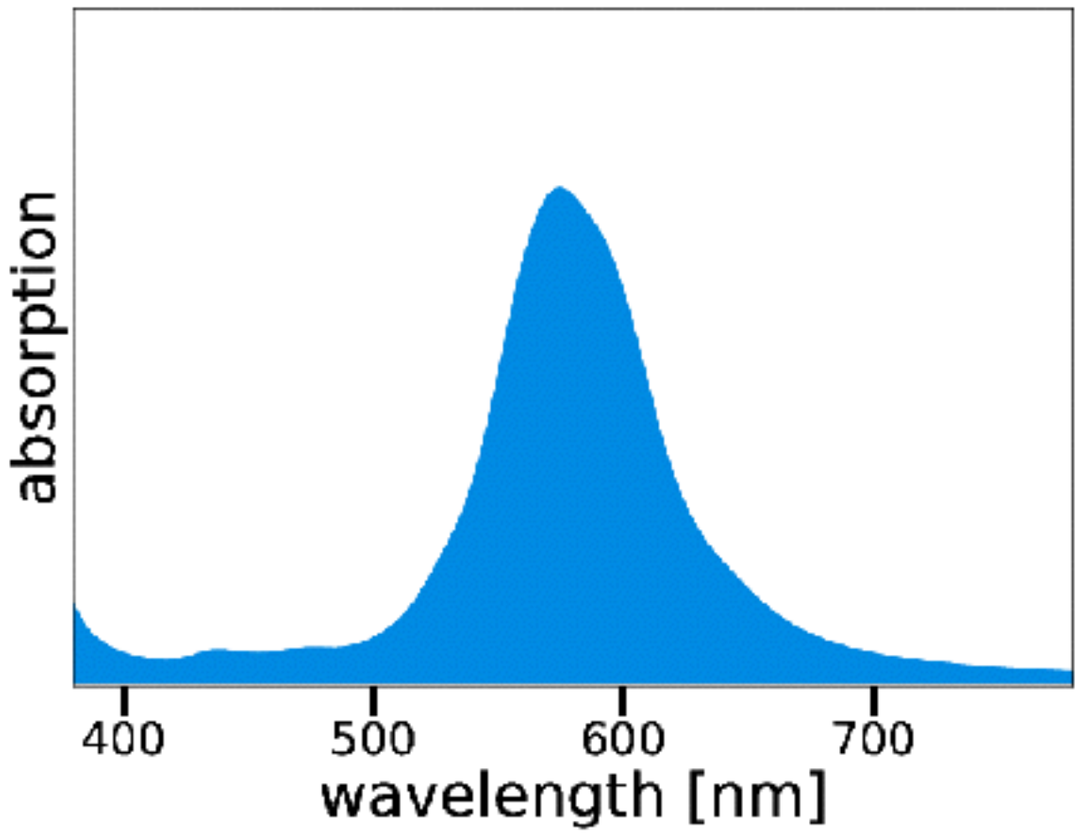


in the quest for a natural *blue 1*

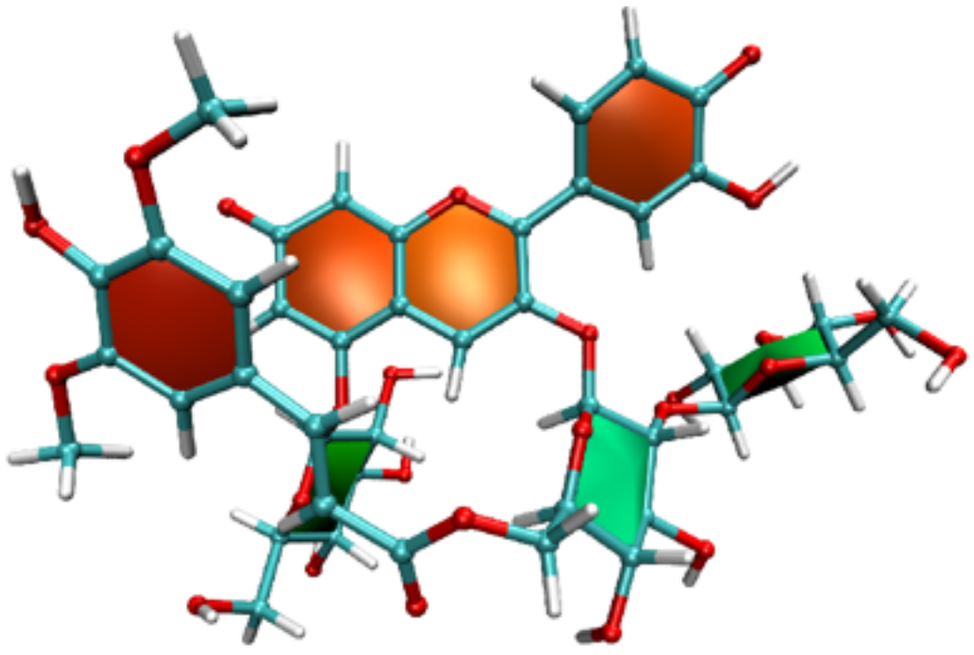


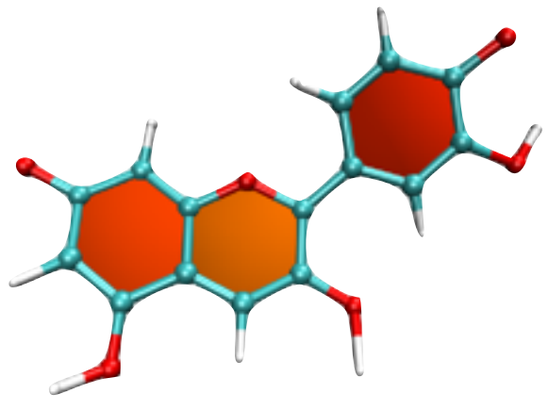


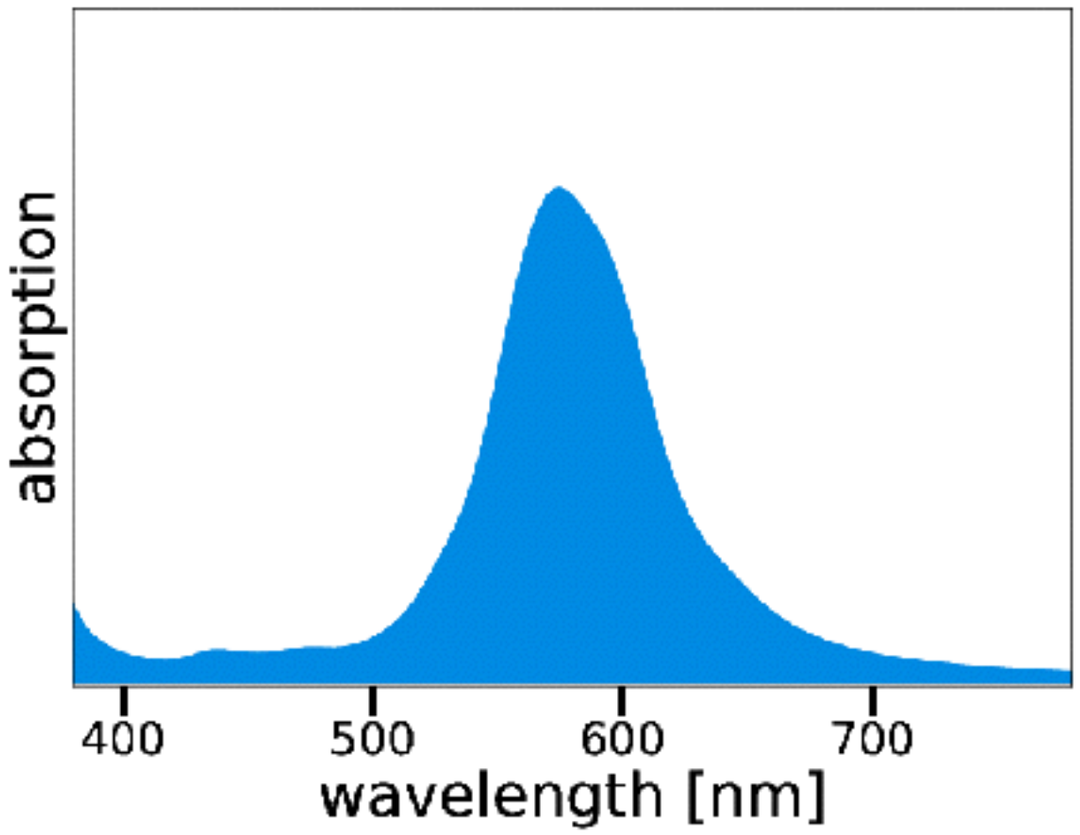


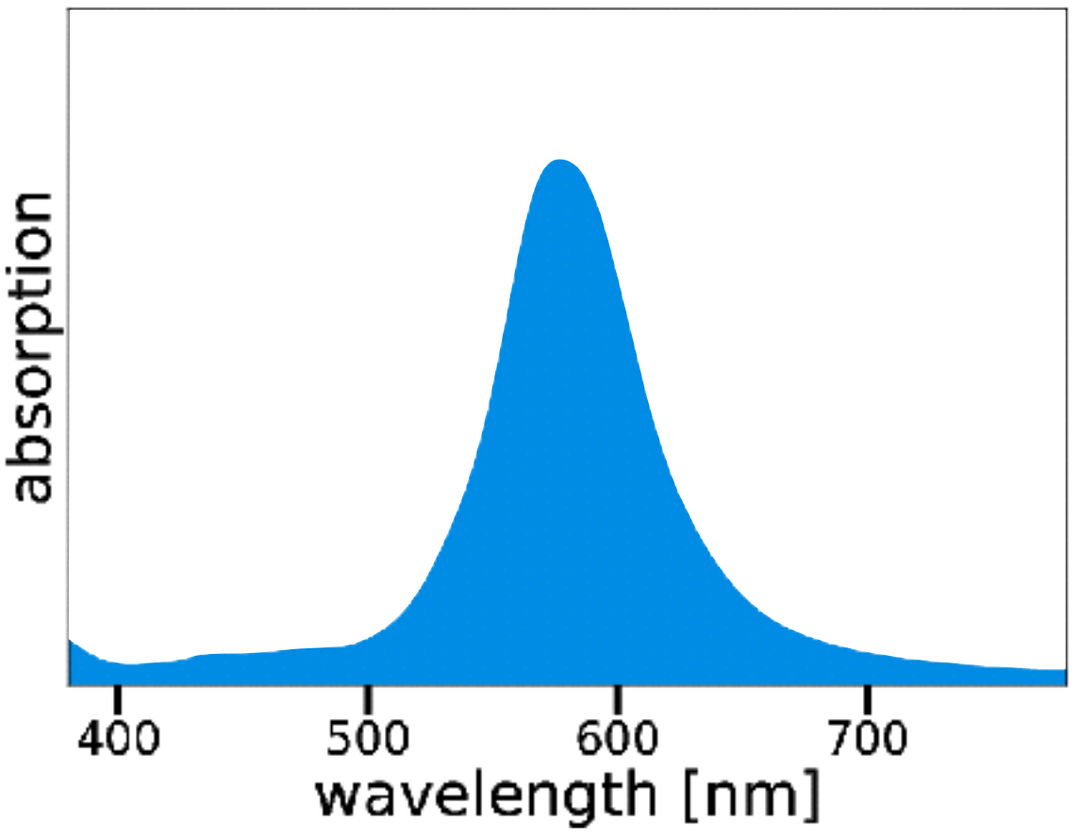


in the quest for a natural *blue 1*

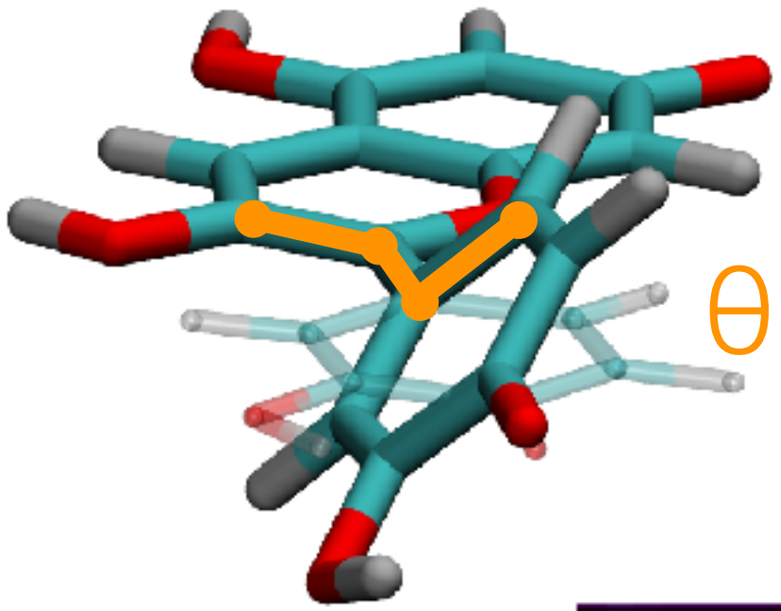


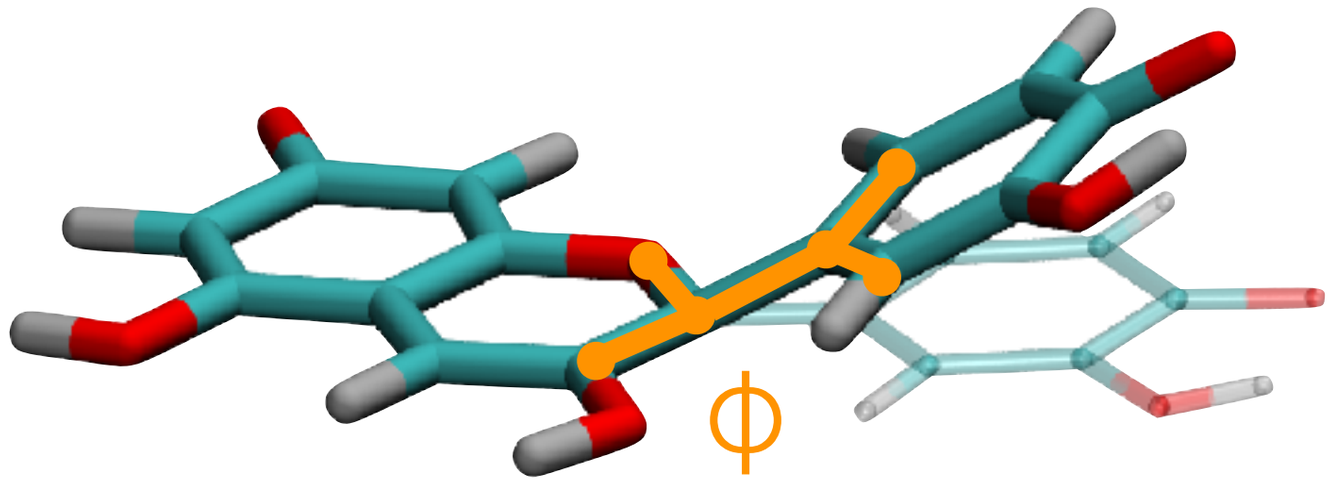


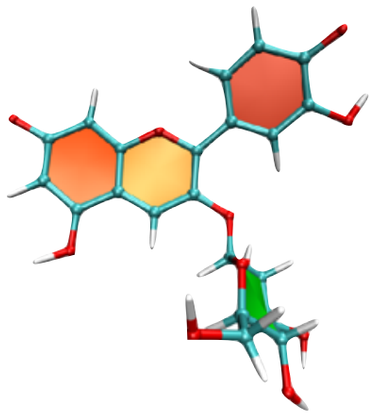


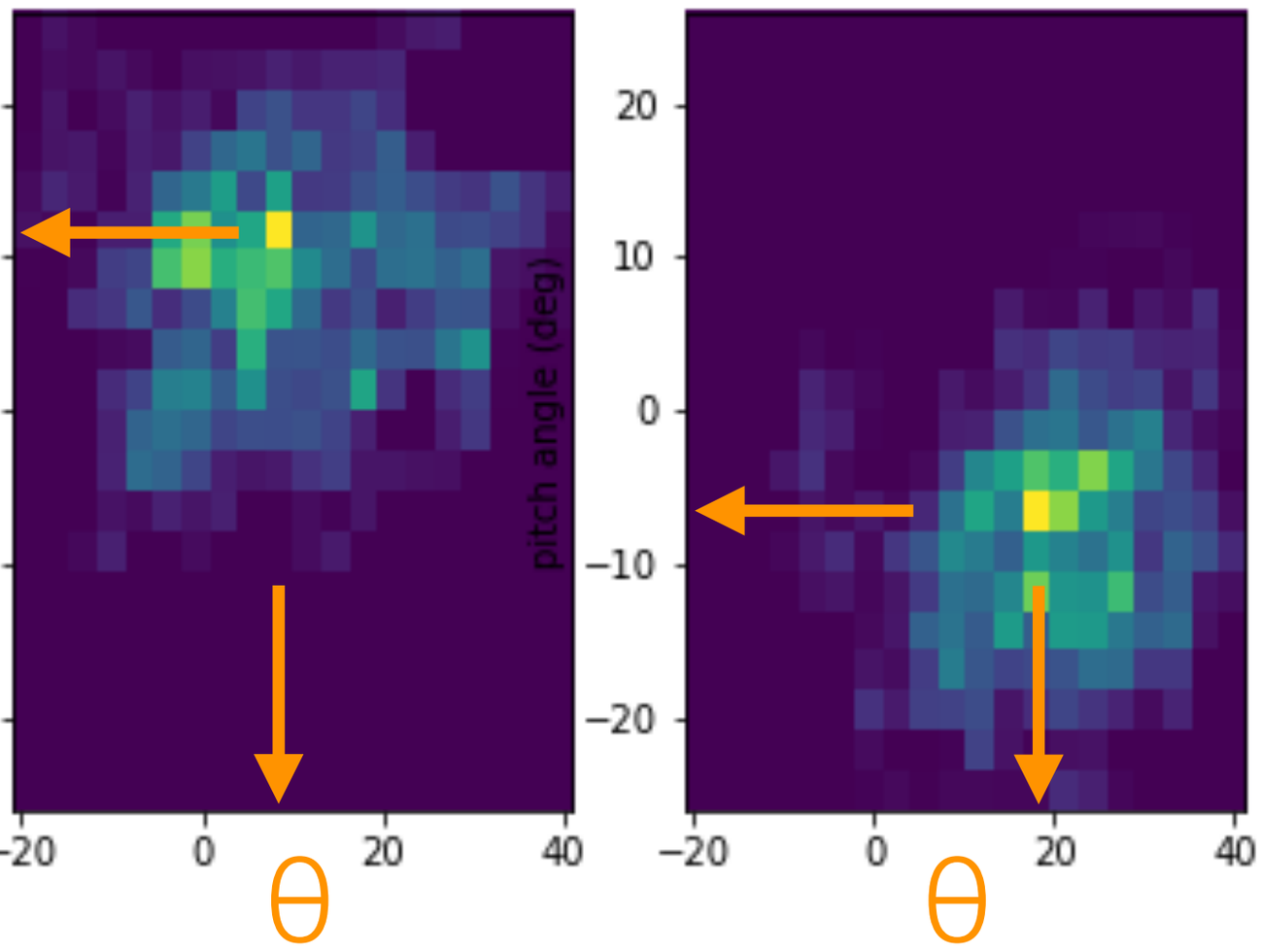


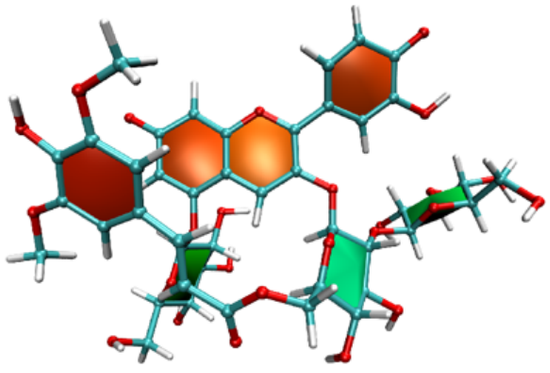
in the quest for a natural *blue 1*



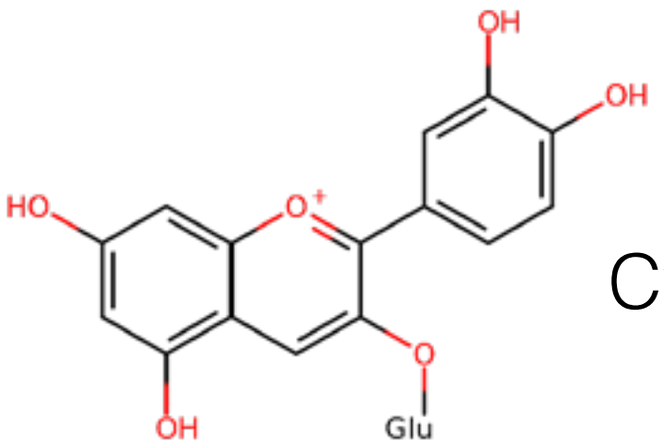






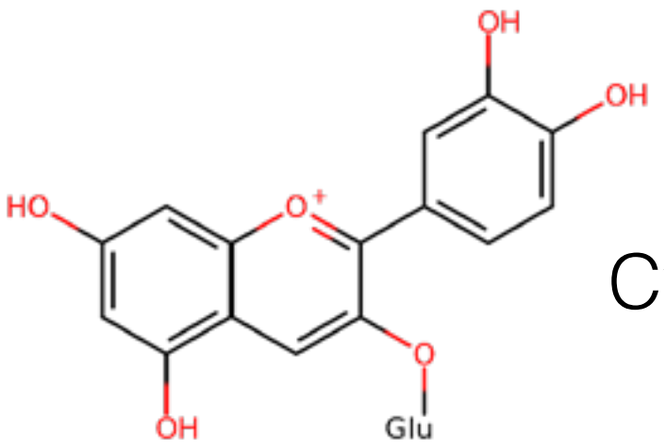


predicting tautomeric equilibria and pK_a



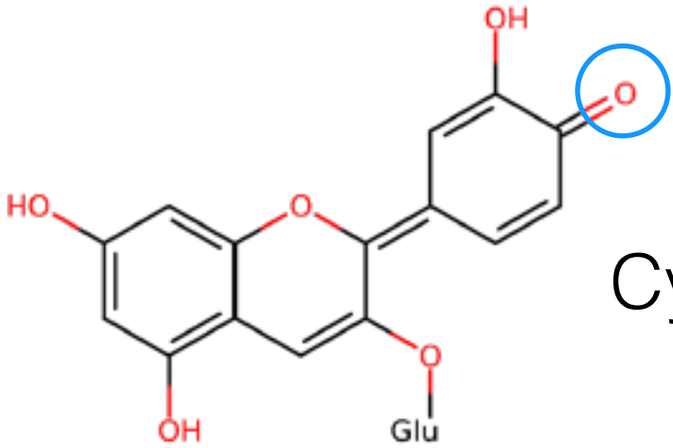
Cy3G+

predicting tautomeric equilibria and pK_a



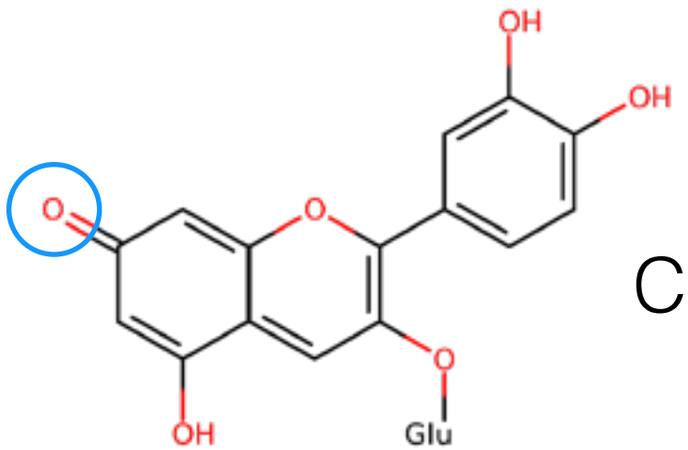
Cy3G+

±H+

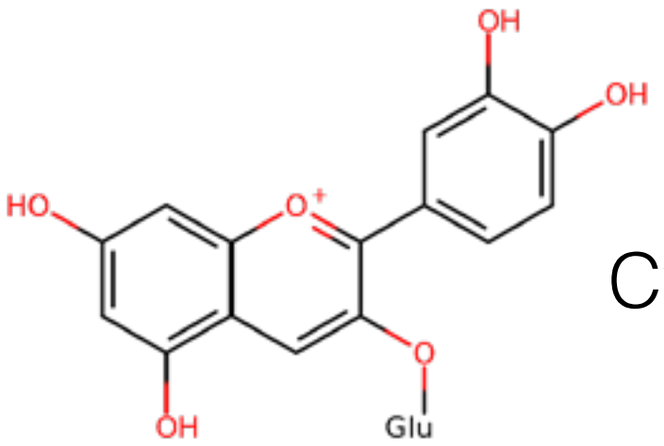


Cy3G (4')

predicting tautomeric equilibria and pK_a

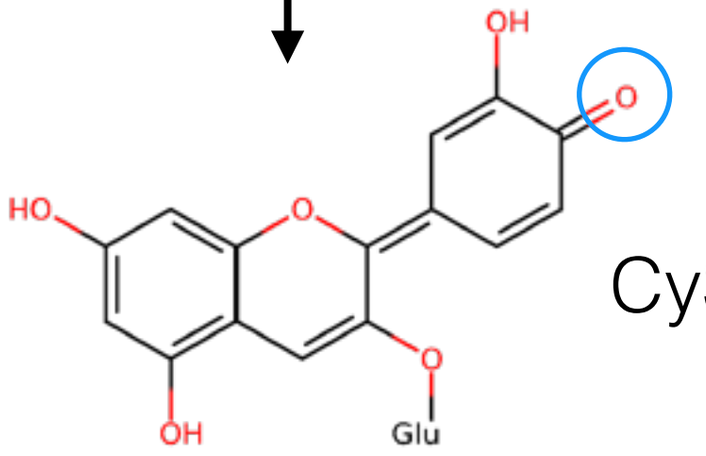


Cy3G (7)



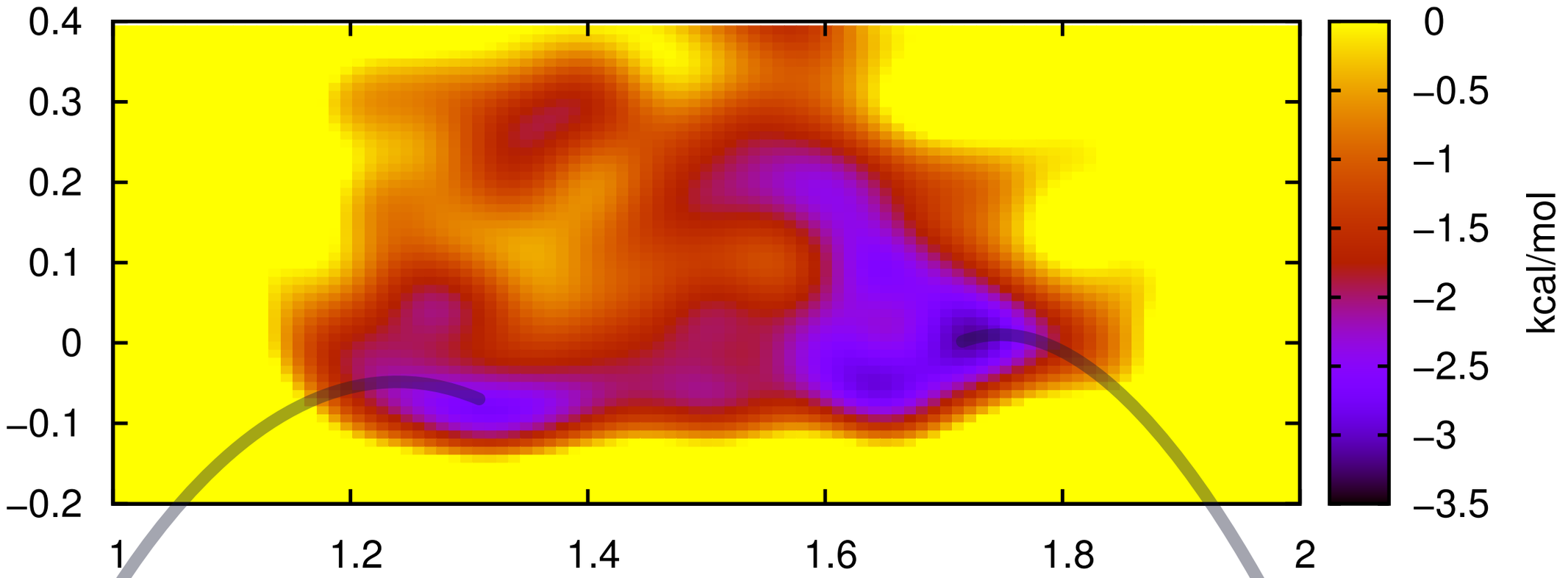
$\pm H^+$

$Cy3G^+$



Cy3G (4’)

predicting tautomeric equilibria and pK_a



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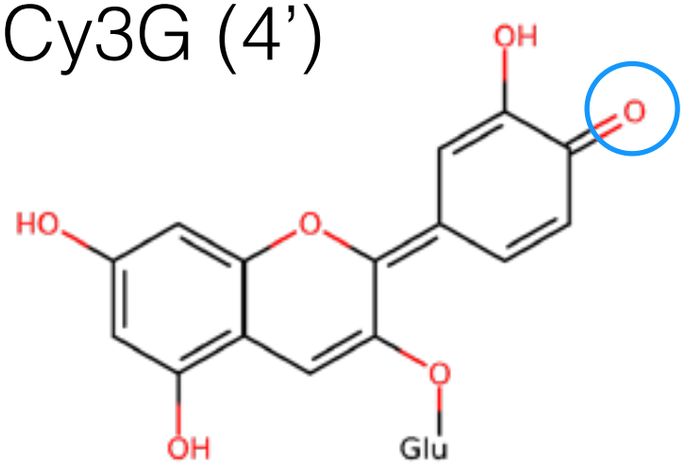
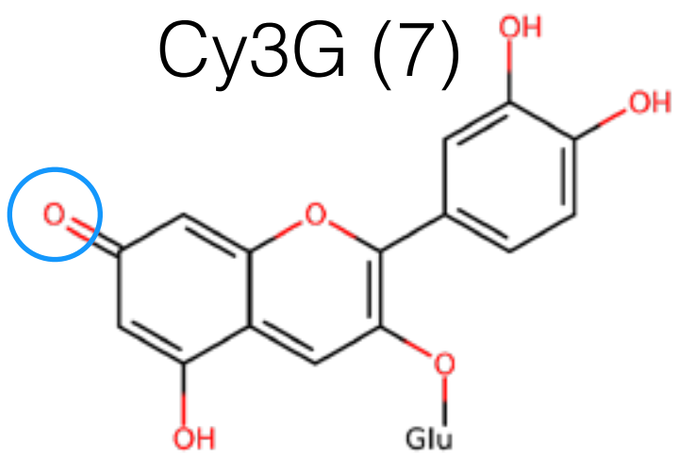
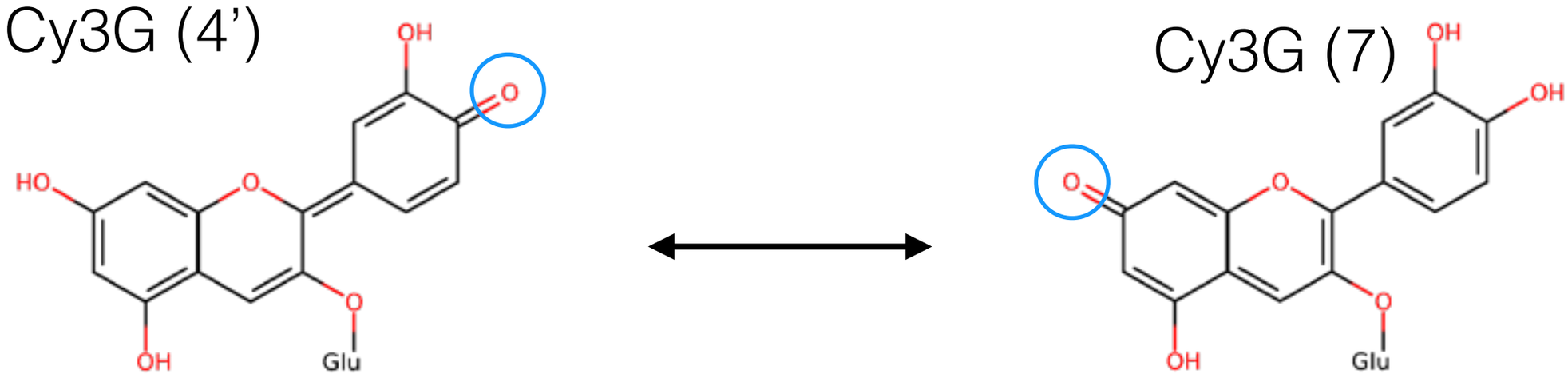


Cy3G (7)



predicting tautomeric equilibria and pK_a



thermodynamic integration

$$\Delta F = \int_0^1 \left\langle \frac{\partial H(\eta)}{\partial \eta} \right\rangle d\eta$$

predicting tautomeric equilibria and pK_a

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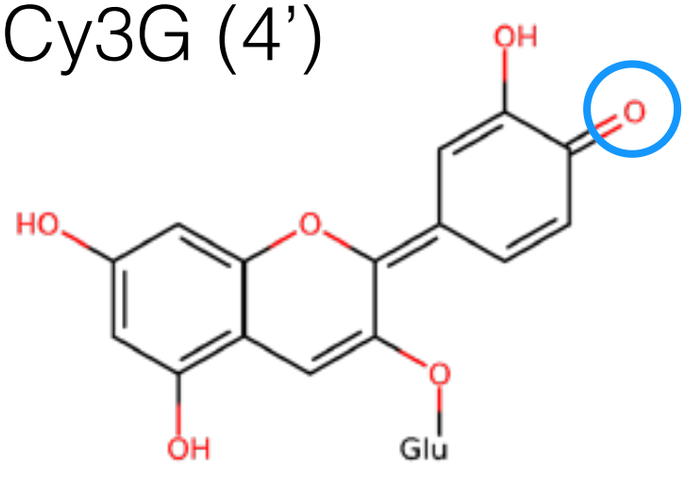
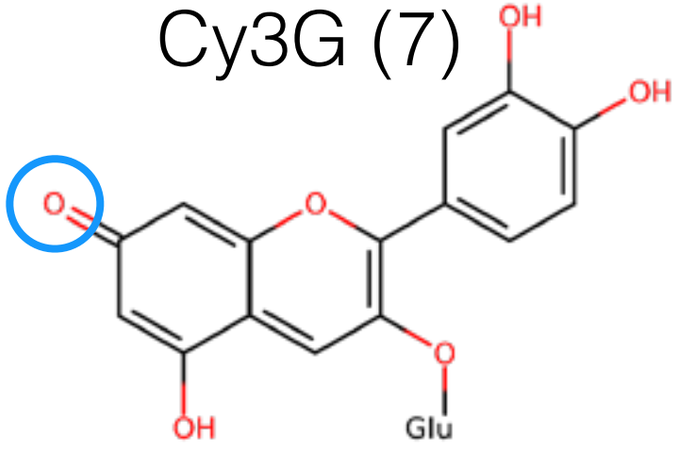
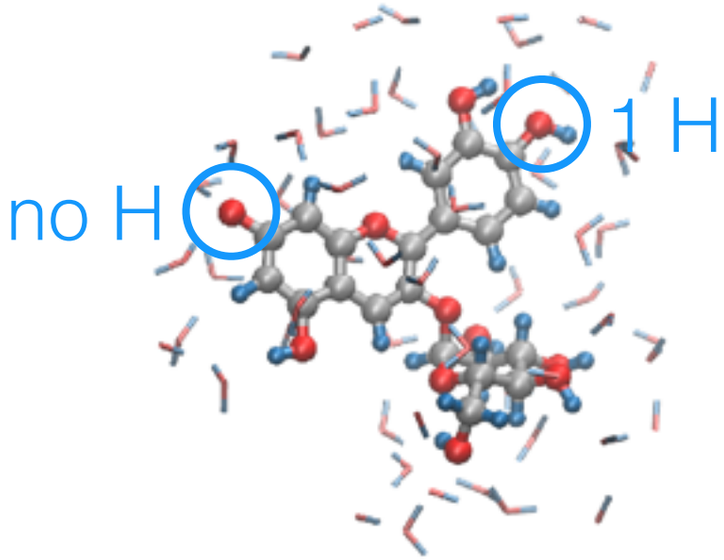
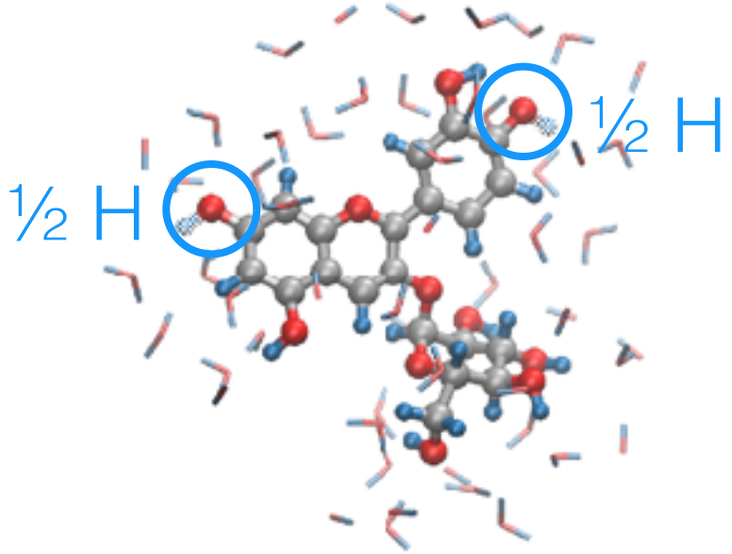


Cy3G (7)

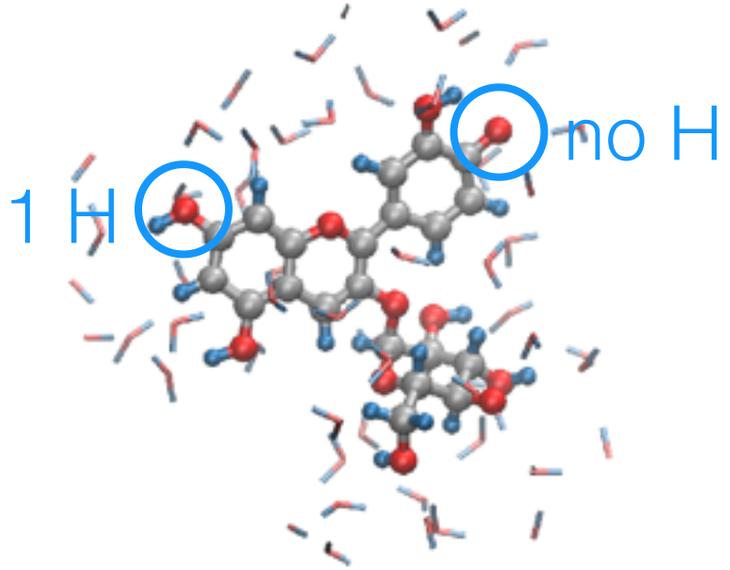




λ=0



λ=½

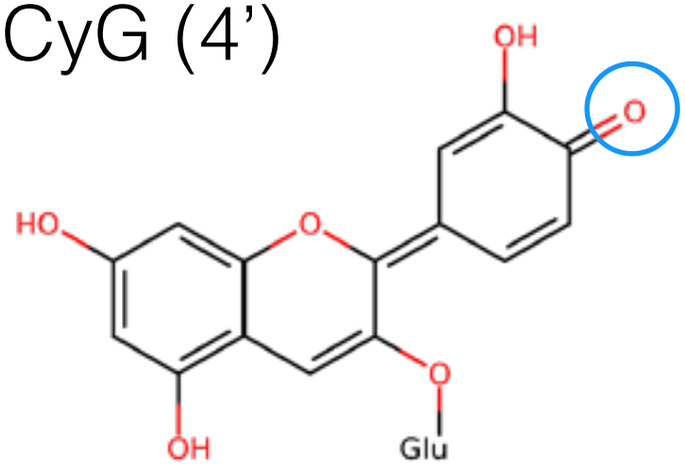


λ=1

$$\Delta F = \int_0^1 \left\langle \frac{\partial H(\eta)}{\partial \eta} \right\rangle d\eta$$

predicting tautomeric equilibria and pK_a

CyG (4')



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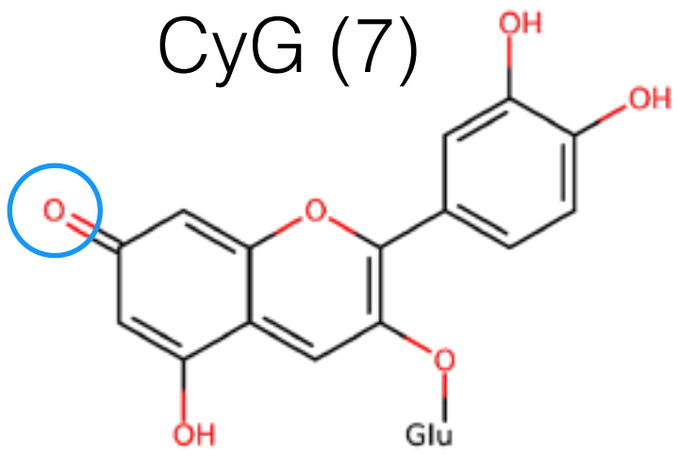

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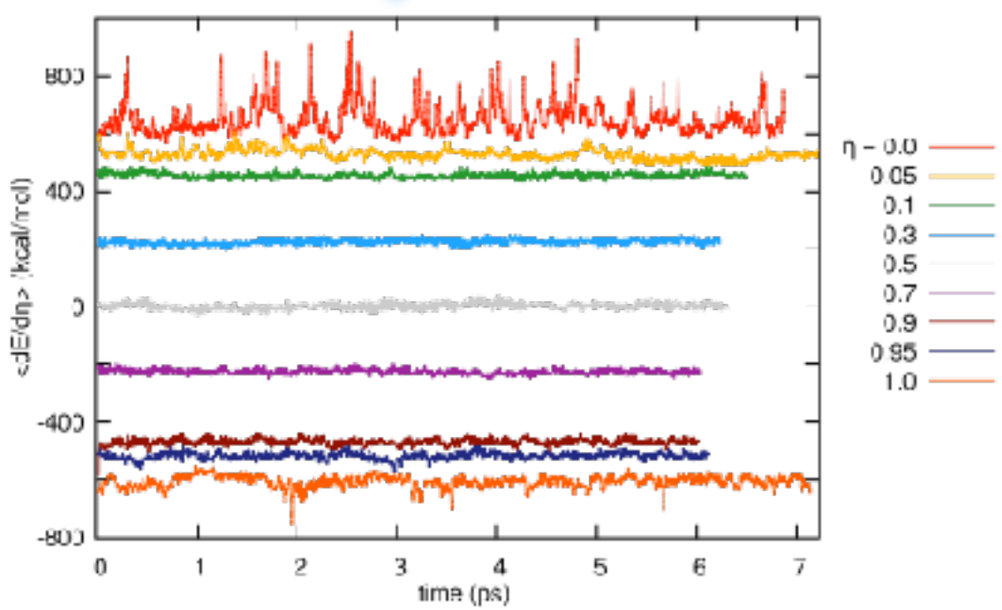

predicting tautomeric equilibria and pK_a

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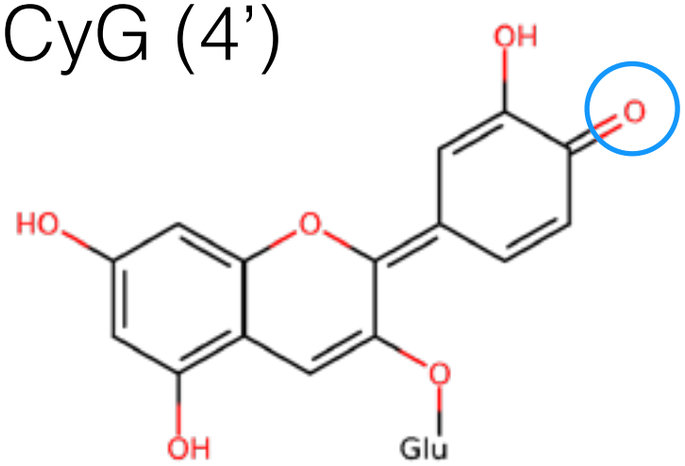

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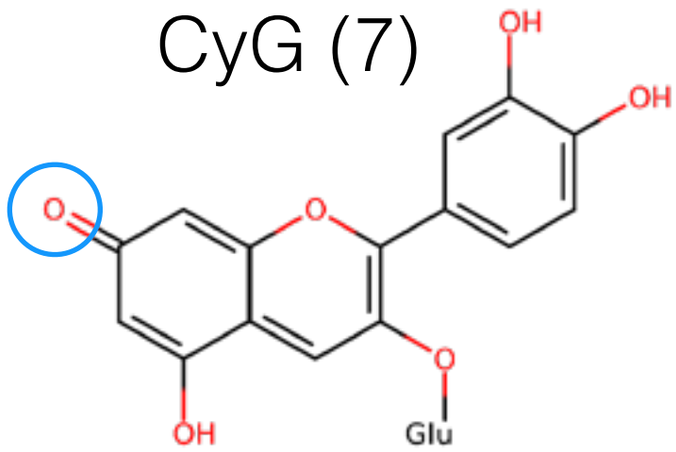

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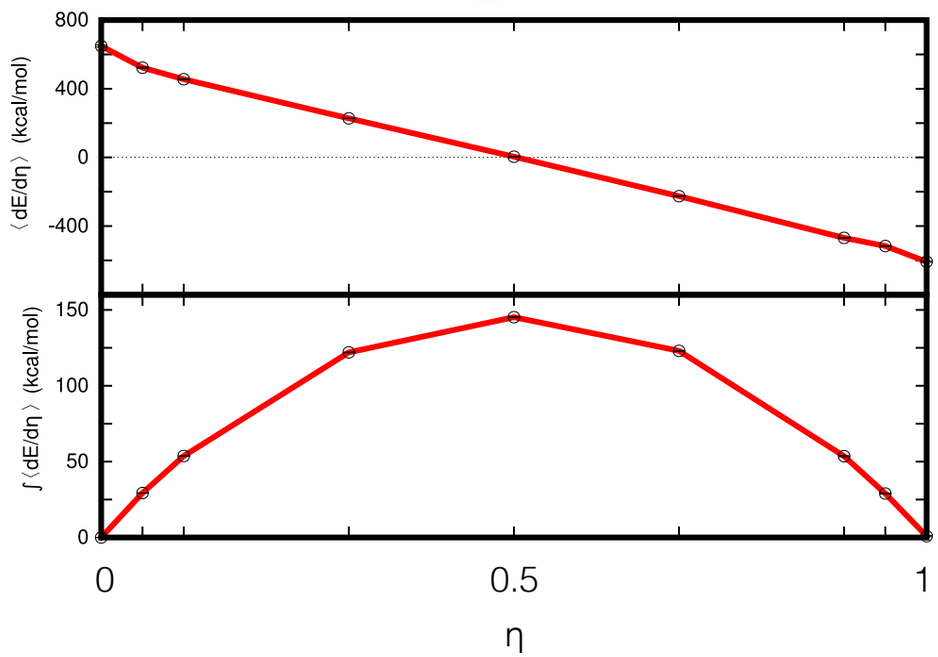

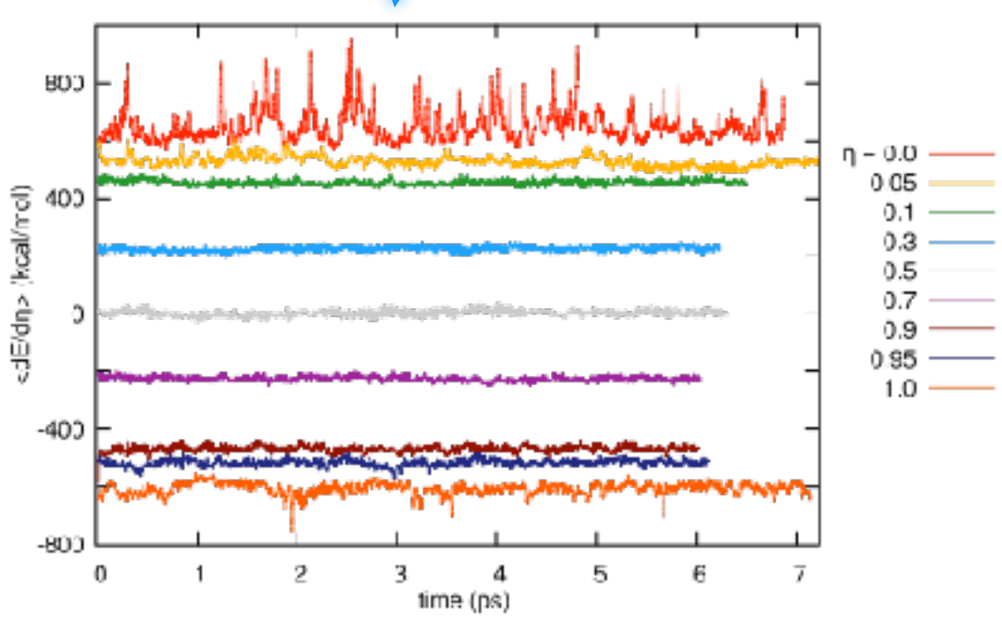

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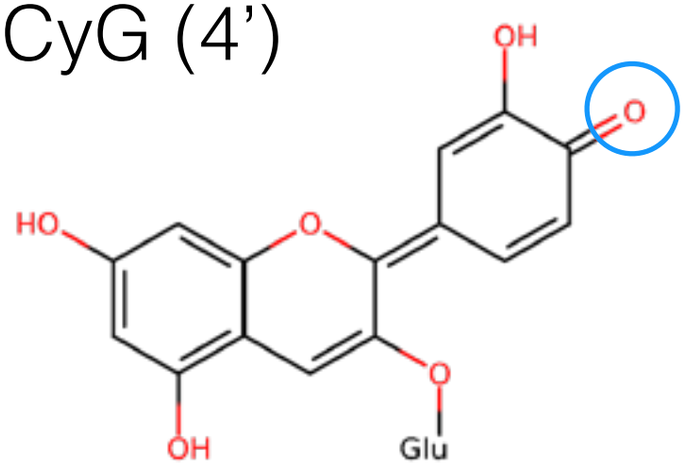
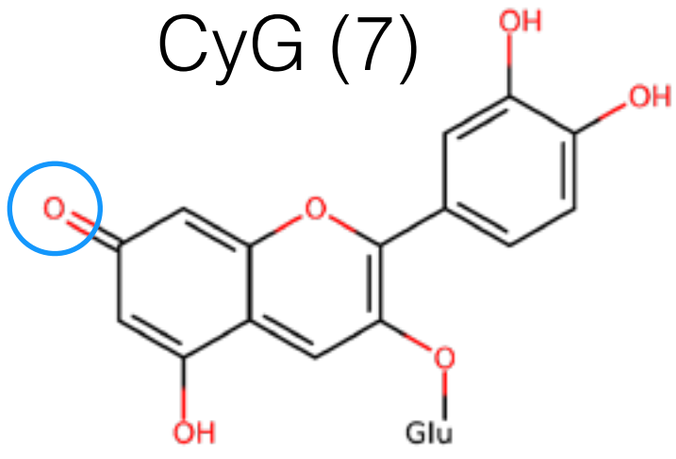


CyG (7)



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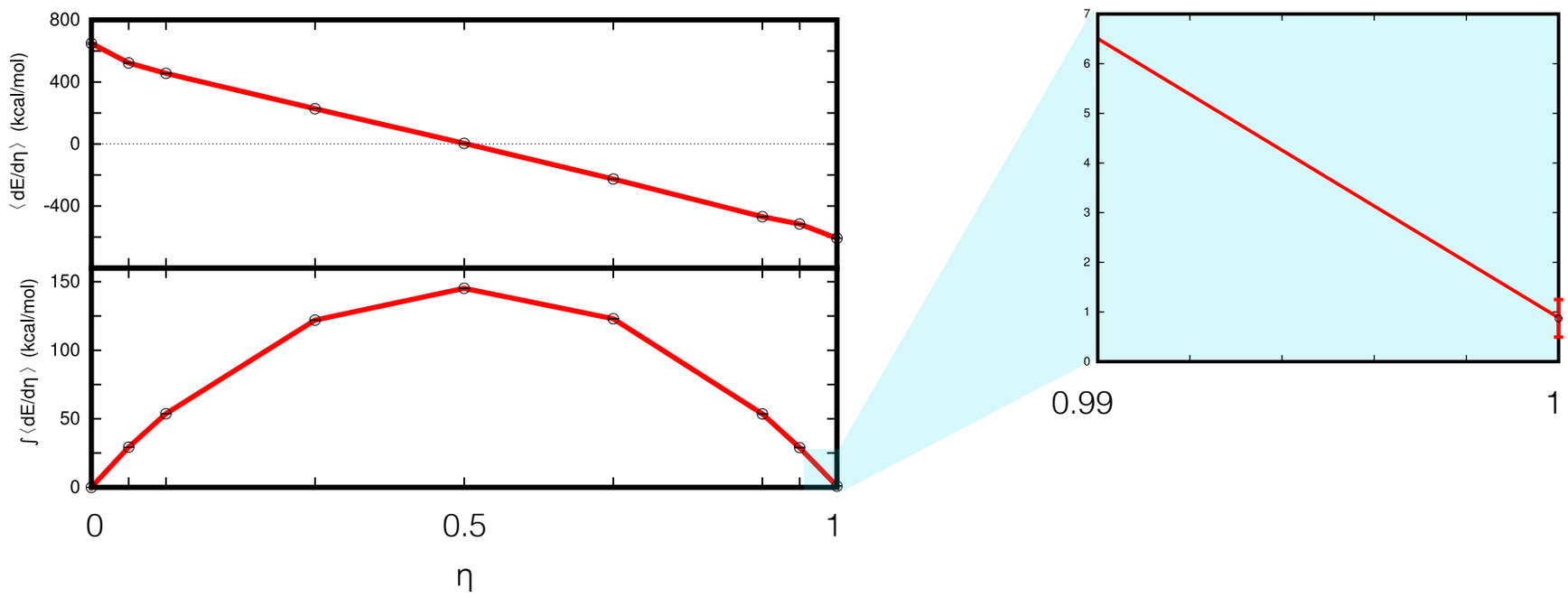

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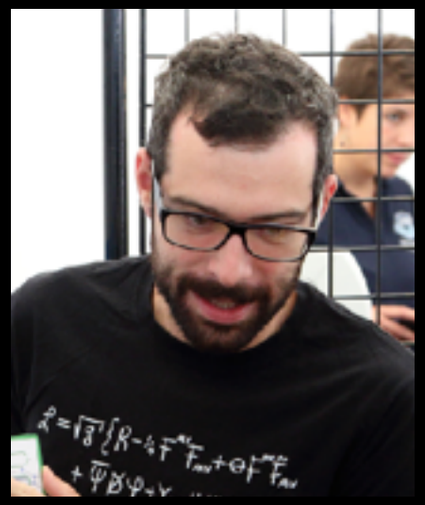
- molecular simulations have been instrumental in the identification of a natural substitute for *blue 1*

- applied research can be fun and instructive for theoretical physicists as well …

thanks to

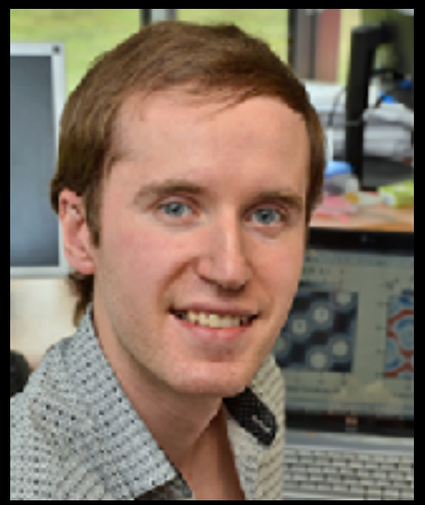
Mariami Rusishvili



Luca Grisanti

Sara Laporte

Alessandra Magistrato



Iurii Timrov

Alessandro Laio

Marco Micciarelli

Marta Rosa

Tom Collins

Rebecca Robbins

and to


MAX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