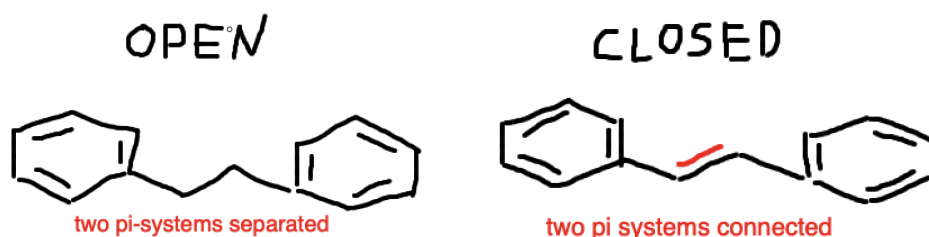


## Your Glasses Are Smarter Than You Think

If you're reading this, chances are you're wearing a pair of glasses or have a pair nearby. About 64% of adults in the United States wear prescription glasses, and many of them also own sunglasses for their versatility and style. None of us got wire-rims after watching *Harry Potter* (2001), but you did see a couple more Ray-bans on the streets after *Top-Gun* (1986). Now, are glasses wearers doomed to sacrifice sight for aesthetics? Experts certainly don't think so. Enter photochromic, or "transition" lenses that put a mysterious blind over the windows of your soul whenever you step outside. How do your glasses "know" when you walk outside?

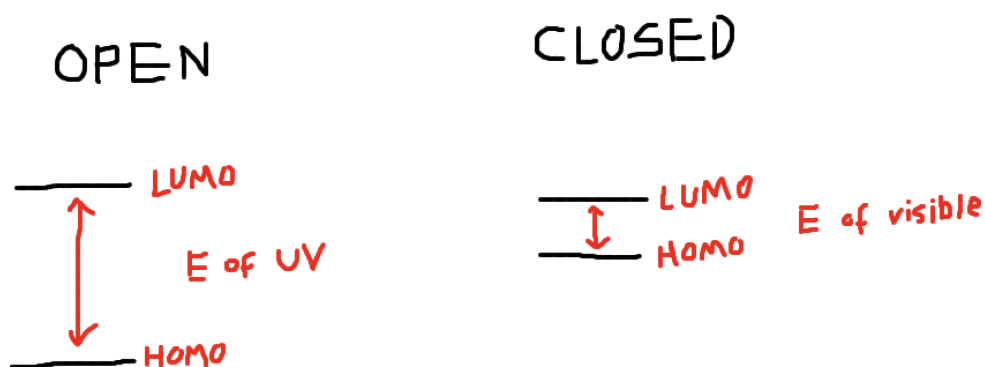
Photochromic lenses are just normal plastic or glass lenses that have been doped with light-sensitive molecules. Indoors they're clear, and in sunlight they automatically darken. Modern photochromic lenses are made of plastic with organic dyes embedded in them. These organic dyes change their shape when they absorb UV light, switching between a clear form and a colored form. You can think of each dye molecule as a window blind. In the "open" position, the lens looks clear and lets visible light through. In the "closed" position, it soaks up part of the visible spectrum, making the lens look dark. UV light flips the blind closed, while heat and visible light flip it back open.



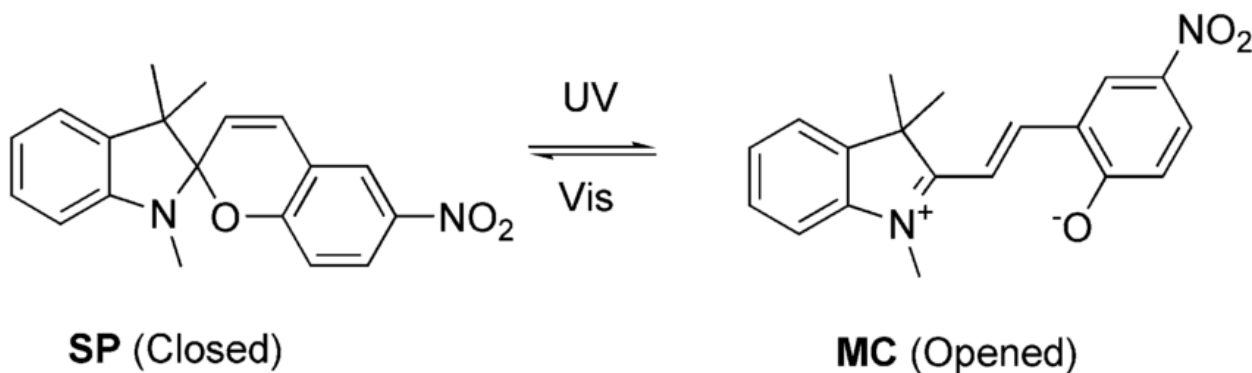
These two positions, or shapes, of the molecule "open" or "closed", have different ways of sharing electrons. In the clear, "open" form, the molecule is bent and the double bonds are isolated from one another. The effect of these double bonds being separated is that it only absorbs light in the UV spectrum and reflects light of all other wavelengths, appearing clear to the viewer. In the dark "closed" form, the molecule becomes more flat and conjugated, meaning that the double bonds are able to share electrons among themselves.

Imagine riding on a bus or the train. At the first few stops, people sit far away from each other. It takes a lot of energy to get up and touch the person closest to you. This is like the closed

position. It takes a high energy light such as UV to be absorbed. As you and I cannot see UV light, we see no visible effect on the lens. As more people get on the bus, spaces between people begin to fill up. At this point, it takes very little energy to touch the nearest person; just move your elbow! This is akin to the open state, where electrons are free to move and interact instead of being confined in their respective bonds. This time, a light of lower energy, such as visible light, is able to be absorbed and we see this as the lens gets darker.

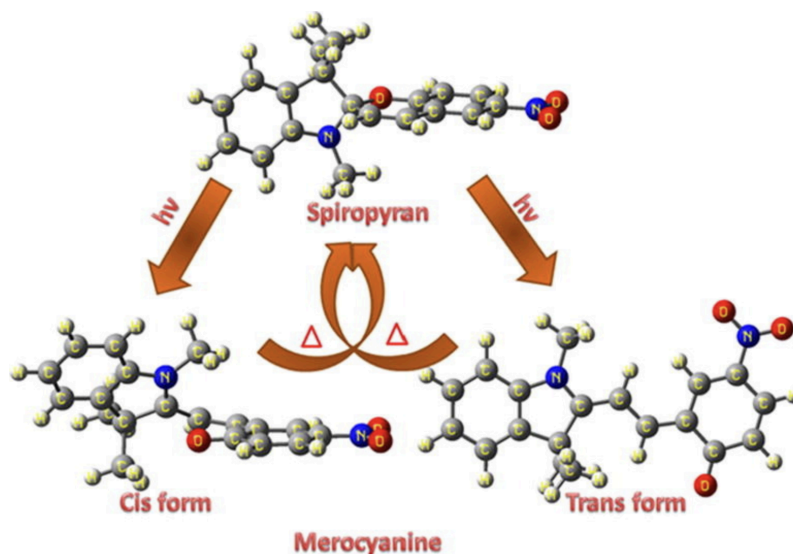


You might also notice that they get dark pretty quickly once you go outside but it takes a couple minutes for it to clear up fully once you're indoors. That is because darkening is driven by UV from the sun. There are a lot of photons hitting the molecules at once, so switching to the "closed" or dark position is fast. The process of clearing up is mostly a thermal one. Each molecule has to find its way back to the lower energy clear shape by itself. This is like everyone trying to get off the bus at the same time, clogging the exit and slowing down the process. Heat helps, which is why your glasses transition much faster in warmer climates compared to colder ones. A summer deboarding where everyone runs into the sunlight is much different than a winter coat congested one as people dread leaving the bus heating system.



Not satisfied with the explanation? Here's one for those of you seeking a deeper dive. Transition lenses are doped with a chemical called spiropyran, a UV activated compound with two forms, an SP "closed" form and a MC "opened" form. Take a look at the SP molecule above. It has a conjugated benzene ring on the left side and a conjugated benzene ring on the right side. Due to the  $sp^3$  hybridization of the carbon in the middle, the two rings sit almost orthogonal to each other, minimizing  $\pi$  orbital overlap and consequently, conjugation. These two separate conjugated systems have high gaps between the HOMO and the LUMO, absorbing high energy light such as UV with wavelengths that we cannot see. This is why the compound appears clear.

UV light causes the promotion of electrons to the C-O antibonding orbital, leading to a heterolytic cleavage of the bond between carbon and oxygen at the chiral center. In this excited state, the molecule undergoes a conrotatory electrocyclic ring opening, giving a twisted cis-merocyanine. The compound is allowed to relax to its ground state and arrives at a planar trans-MC conformation. Observe how the two benzene rings are connected through atoms that are  $sp^2$  hybridized. This planar conformation aligns the  $\pi$  orbitals and allows the two rings to "talk" to each other in conjugation. This system of delocalized electrons decreases the HOMO and LUMO gap to the lower energy, visible range. This intense, visible absorption is what gives the transition lens its classic dark color. The process of backconversion is the reverse electrocyclic ring closure, which breaks the conjugation. Depending on the solvent, or characteristics of the glasses, and substitutions on the compound, the lifetime of this MC compound varies from microseconds to hours.



There are a couple different ways to tweak the characteristics of this compound. The longer the conjugated pi system is in the MC form, the lower the HOMO-LUMO gap, shifting absorption towards red. However, the longer system cannot come at the expense of its planarity, as a twisted molecule decreases effective pi orbital overlap and shifts absorption back towards blue. In this way, substituents that sterically hinder full planarity will limit color depth. In order to keep the electrons flowing in such a long conjugated system, substituents can push and pull electrons through the system. Many MC molecules have a strong donor end with O<sup>-</sup> and a strong acceptor end with a quaternary N<sup>+</sup> end. The greater the difference between donor and acceptor strength, the greater the polarization of the molecule and the compound can absorb more red. Putting electron donating groups such as -OMe on the donor ring and putting electron withdrawing groups such as halogens on the acceptor ring will both shift the absorption red.

A little lost? Don't worry, your glasses will work regardless if you understand pericyclic reactions or not. Transition lenses are a cool and functional result of chemical research. From glass doped with silver-halide to plastic lenses with organic molecules in them, people are always finding ways to use chemistry to make the world a better place.

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