

Chlorophyll has unique photophysical properties - a first excited singlet state (S1) at the energy embodied by red light, and a second excited singlet state (S2) at the energy embodied by blue light. It is extremely rare for organic molecules to have high rates for useful photochemical processes (at the reaction center Chl pair) and low rates of loss by internal conversion (to heat) or intersystem crossing (to the first excited triplet state, to which direct absorption is first-order forbidden by quantum symmetry rules, and with which there is a danger of creating damaging singlet oxygen from ground-state triplet O₂). G. Wilse Robinson at Caltech had a great course on this topic, using a sophisticated analysis of the density of states (rovibronic states, or quantum energy levels). I wrote about this years ago - see V. P. Gutschick. 1978. Concentration quenching in chlorophyll-a and relation to functional charge transfer in vivo. *J. Bioenerg. Biomembr.* 10: 153-170. Note that absorption spectra are broadened by local environmental interactions of the Chls to cover a good fraction of the solar spectrum, and also there are auxiliary pigments (carotenoids) to fill in even more of the spectrum. Absorbing 85% of the solar spectrum is a good deal! Remember, too, that overstory plants spend a lot of time light-saturated, so that not absorbing too much light (and thus, not getting too much photodamage, with the help of xanthophyll dumping of excess absorbed light) is a good thing. Light saturation could only be avoided by having even bigger investments in Rubisco, and that's insupportable of the basis of total energetic cost of making leaves (see also V. P. Gutschick. 1984a. Photosynthesis model for C₃ leaves incorporating CO₂ transport, radiation propagation, and biochemistry. 1. Kinetics and their parametrization. *Photosynthetica*. 18: 549-568, and V. P. Gutschick. 1984b. _____. 2. Ecological and agricultural utility. *Photosynthetica* 18: 569-595. Thus, getting good photochemistry). So, getting good photochemistry means taking the best molecules (Chl a and b) that evolved. Interestingly, we've all seen publications about the possibility that there are better Rubiscos, but I haven't seen articles about better Chls, other than having stacked systems, one using red and blue and the other using green....but, again, too much light absorption is a more common problem than too little, in most environments. Using Rubisco more efficiently in C₄ plants vs. C₃s is a partial solution for warm regions - not a universal solution.

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Why are plants green? - ResearchGate. Available from:
https://www.researchgate.net/post/Why_are_plants_green [accessed Jan 22, 2017].