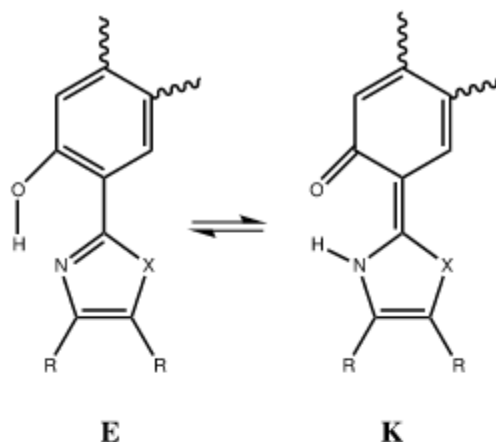
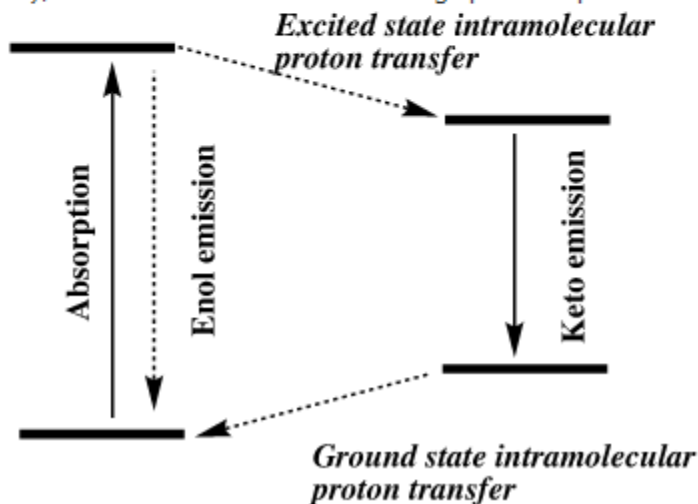


## Molecule-sized pixels

The ultimate reduction in size for an engineer is to a single molecule. It's been [done for a car](#); now it has been reported for the pixel (picture-element).<sup>[1]</sup>



The molecule above ( $X=O$ ,  $NR$ ,  $R=aryl$ , etc) has been shown to be capable of acting as a molecular pixel. To give some idea of the reduction in size, computer displays currently only squeeze 400 or so pixels into an inch (the archaic, but common units used to measure pixel sizes). The secret to engineering this is to prevent energy transfer occurring between adjacent pixels (= molecules on this scale), and this has been done using quite simple chemistry!



The concept is to allow a molecule to reach an excited state by photon absorption, but to prevent emission from occurring (which would result in energy transfer to adjacent molecules) by inducing a rapid change in the molecular structure of the excited state. This reaction has to be very fast, and one of the fastest reactions is the intramolecular proton transfer. In this example it converts the enol form of the oxazole **E** to the keto form **K**. On the ground state surface, prior to excitation, the enol form is

the lower in free energy (retaining the aromaticity of the phenyl ring). The basis of the molecular design is to find a molecule where it is the keto form that is lower in energy on the excited state surface, such that the *excited state intramolecular proton transfer* is both fast and in effect irreversible. In the keto form, any emission down to the ground state is now incapable of energy transfer to adjacent molecules (which are presumed to be still in the ground state and hence the **enol** form).

This sort of system is perfect for designing with the help of quantum calculations, and to give just a hint of how this could be done, I thought I would illustrate how the energetics of the ground and excited states could be quickly obtained to show that the above energy diagram really does apply to these molecules (R=H, X=O). At the  $\omega$ B97XD/6-311G(d,p)/SCRF=chloroform level, the enol[2]<sup>‡</sup> is 11.4 kcal/mol **lower** in free energy than the keto form[3]. A vertical (non-adiabatic) excitation to the first excited singlet now produces a system where the enol[4] is 3.9 kcal/mol **higher** than the keto form[5], which reflects the above diagram exactly.<sup>†</sup>

It is easy to see now that variation in R, X or other parts of the molecule could be rapidly scanned computationally to find out how such variation alters these relative energies. Computational tuning could then be used to *e.g.* optimize avoidance of energy transfers between adjacent molecules (pixels) and no doubt to also predict the actual absorption energies (*i.e.* colours) of new candidate molecules.

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<sup>‡</sup>Here I introduce the use of the so-called "**short-doi**". The data citations above refer to the Figshare repository, the first citation of which takes the long form <http://dx.doi.org/10.6084/m9.figshare.769259> By invoking <http://shortdoi.org/10.6084/m9.figshare.769259> one can obtain the short form <http://doi.org/nd9>, of which the essential part, **nd9**, is now just 3-characters long. This form might be an alternative to QR-codes in **e.g.** lecture slides and other media where the human has to remember the value. In a machine-sense of course, the short form offers no advantage over the long form.

<sup>†</sup>Strictly speaking, one should locate the conical intersection for proton transfer on the excited state, but the above calculations take only minutes literally, whereas locating a conical intersection is a rather more complex task.

**Source:** <http://www.ch.imperial.ac.uk/rzepa/blog/?p=10990>