

Electricity from Light: A Novel Light-Harvesting Molecule

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Aims

- To synthesise a new molecule which can efficiently convert energy from light to an electrical form.
- To test the molecule for a *charge transfer* process.

Background

The use of solar energy as an alternative fuel is increasingly important. Solar fuel cell devices require efficient light-harvesting materials. Natural photosystems, such as chlorophyll in plants, are highly efficient at absorbing light and converting it to usable forms of energy. This research focuses on mimicking such a system by using the organic dye called **dipyrin**. This is present in the new compound as it has excellent light absorption properties in the visible spectrum and has a similar structure to porphyrin, the basic building block of chlorophyll.



Figure 1: The new compound (RM₃) in visible light (left) and shown fluorescing in UV light (right).

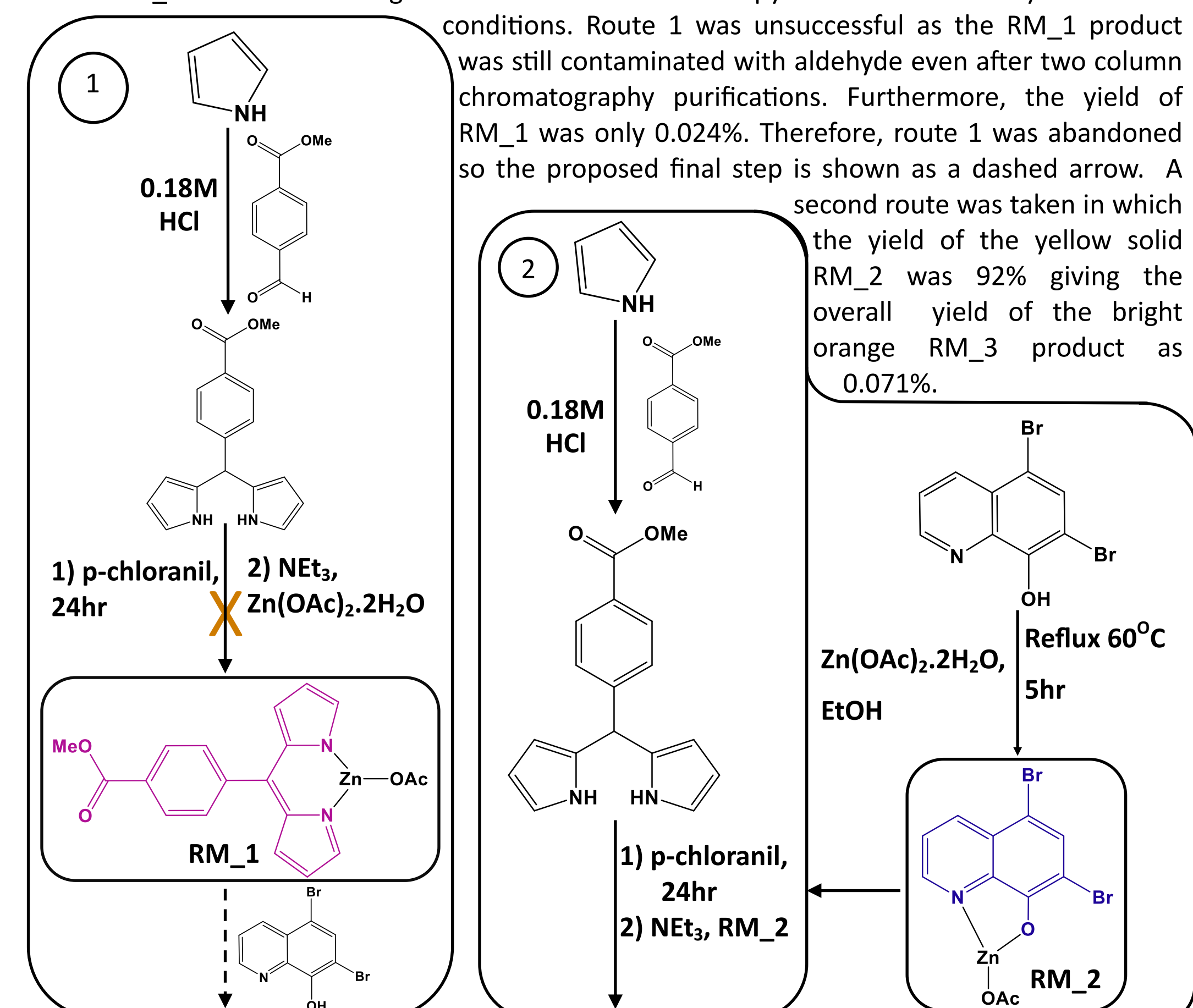
The new compound contains this **dipyrin** and another species called **quinolinolate**, both bonded to a zinc (II) centre. This presents the possibility that energy absorbed by the **dipyrin** species will be transferred to the **quinolinolate** in what is called a charge transfer process. This mechanism may increase the range of the wavelengths the molecule can absorb and emit and could thus make it more useful in its potential applications. The unique study of this mechanism is the 2nd aim of this project.

Real World Applications

- In most potential applications the new molecule would be contained in a nanomaterial scaffold, such as silica, to provide a more stable material with tuneable optical properties. Therefore, subsequent research would first involve the incorporation of the compound into a porous silica framework.
- As a molecular dye the compound could have use in a dye-sensitised solar cell (DSSC), in which molecular dyes on the cell surface absorb light and transfer photo-excited electrons to titanium dioxide, from which electricity can be generated.
- Furthermore, molecular dyes are used in photonic antenna systems where they collect light for artificial photosynthesis.

Method

The below schematic represents the 2 synthetic routes planned to produce the new molecule, named RM₃. Both routes begin with the combination of pyrrole with an aldehyde in acidic conditions. Route 1 was unsuccessful as the RM₁ product was still contaminated with aldehyde even after two column chromatography purifications. Furthermore, the yield of RM₁ was only 0.024%. Therefore, route 1 was abandoned so the proposed final step is shown as a dashed arrow.



A second route was taken in which the yield of the yellow solid RM₂ was 92% giving the overall yield of the bright orange RM₃ product as 0.071%.

Conclusions and Discussion

Conclusions

- Synthetic route 2 was much more successful than route 1 and was reproduced once more.
- The emission spectrum shown in figure 2 suggests that RM₃ has been successfully made as the peaks correspond with those from similar compounds in the literature.^{1,2}
- The evidence for charge transfer is limited and further research is needed to come to a definitive conclusion about its presence.
- Figure 3 shows that RM₃ is highly sensitive to the polarity of its solvent.

Charge Transfer

When the compound is exposed to light, its electrons are excited by the light energy. The electrons gain energy and in doing so are promoted to occupy higher energy levels. These electrons then return to their initial level and thus lose this energy which is emitted as light. This is what gives the molecule fluorescence. This process is represented in figure 4.

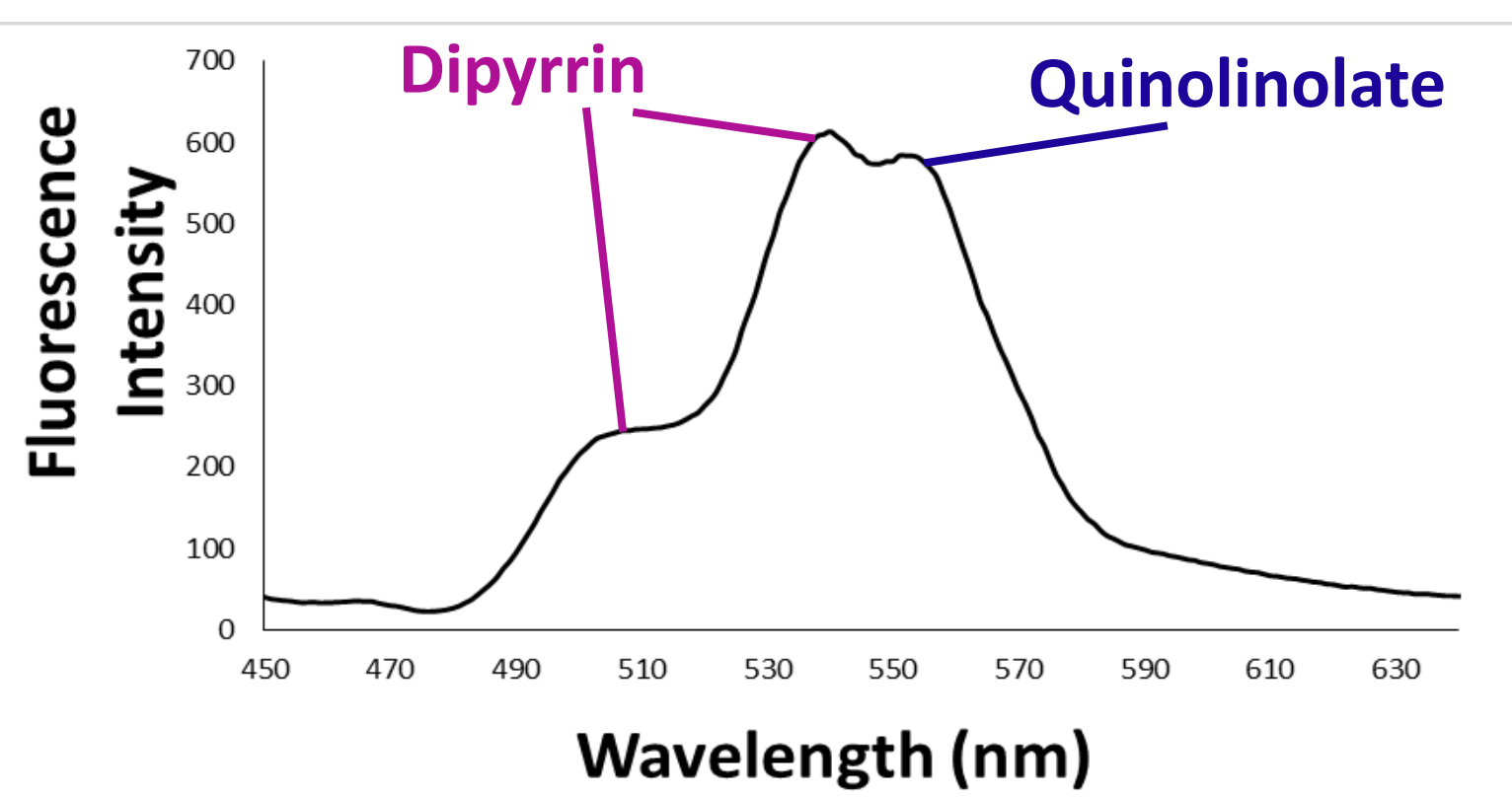


Figure 2: An emission spectrum of RM₃ (0.15mmol.dm⁻³) recorded in acetonitrile. The two peaks at 511nm and 540nm are due to the **dipyrin** emission and the peak at 554nm is due to the **quinolinolate** emission.

The energy and intensity of the emitted light is recorded in an emission spectrum such as that shown in figure 2. The x-axis gives the energy of the light as a wavelength. The smaller the energy gap between the electronic energy levels, the lower the energy of the emitted light and the more the peak is displaced to the right of the spectrum towards lower energy and longer wavelength.

Intraligand (IL) electronic transitions are those which occur separately within each of the **dipyrin** and **quinolinolate** species. Contrastingly, charge transfer is an electron transfer from one species to the other, across the compound. As shown in figure 4, in charge transfer the electrons are promoted from the **dipyrin** lower level to occupy a higher energy state in the **quinolinolate** upper level. The energy gap for this process is smaller than each of the IL energy gaps. Therefore, the light emitted post charge transfer will be of lower energy than the light emitted from each of the IL transfers. Thus, a charge transfer process would be revealed by the presence of an extra peak in the emission spectrum, at a lower energy (and longer

wavelength) than those peaks due to the IL transfers. In figure 2, there is no significant extra peak at a lower energy than those peaks due to the **dipyrin** and **quinolinolate** IL transfers. Therefore, this evidence suggests that charge transfer does not occur. However, charge transfer states can be easily quenched by solvent vibrations in solution and thus the process may not be revealed in this particular spectrum.

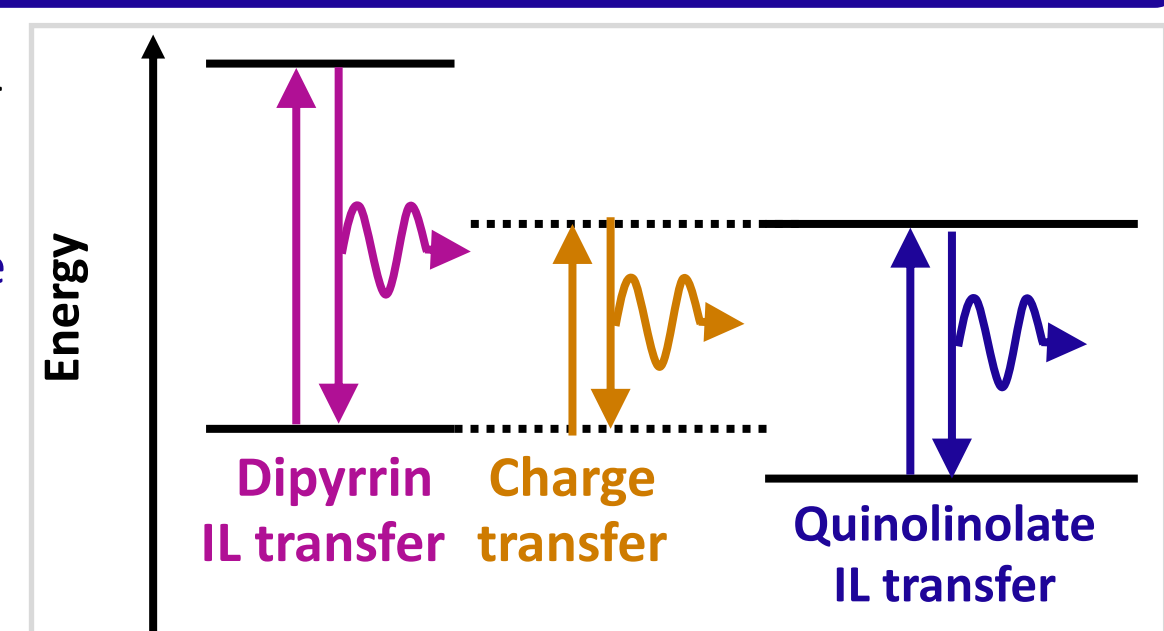


Figure 4: A representation of 3 possible electronic transitions within the compound. The arrows show the transfer of electrons. The horizontal lines represent the lower and upper energy levels.

The Effect of Solvent Polarity

Figure 3 shows that as the solvent polarity increases, the wavelength of maximum emission also increases. In DMSO, the most polar solvent of the three, the wavelength of the peak is at 554nm, indicating a **quinolinolate**-based emission. Contrastingly, in DCM, the least polar solvent, the wavelength of the peak is at 526nm indicating a **dipyrin**-based emission.

The spectrum taken in acetonitrile has an intermediate emission as acetonitrile has a polarity between that of DMSO and DCM. This suggests that an emission centred on the **quinolinolate** is favoured in solvents of high polarity whilst that centred on the **dipyrin** is favoured in solvents of lower polarity.

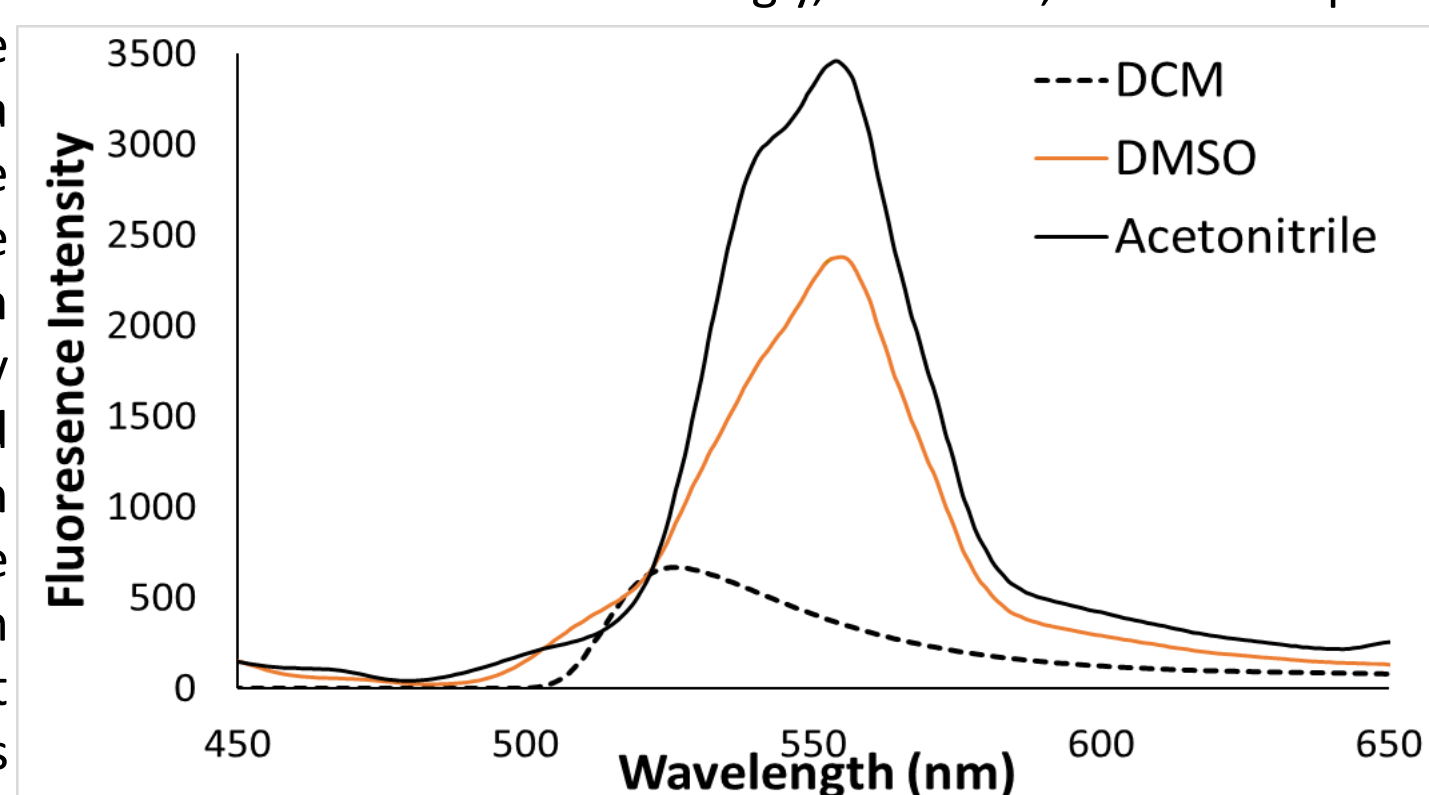


Figure 3: Emission spectra of RM₃ (0.75mmol.dm⁻³) in 3 different solvents.

Such effects can be explained if we consider what happens upon light absorption: when an intraligand transition occurs, the electron density of the whole molecule becomes more polarised, so the molecule is more sensitive to changes in solvent polarity. The **quinolinolate** portion of the molecule is even more sensitive than the **dipyrin** one, so that in DMSO, the most polar solvent, its contribution to the emission is predominant. This phenomenon is called solvatochromism, a change in colour depending on the solvent, and in this case leads to what is defined as red-shift, when the emission energy is pushed into the red region of the spectrum.

Furthermore, the way this spectrum shows both species having changeable dominance in the emission, suggests that they may be linked by a charge transfer process. Again, however, more evidence would be required to prove this, in what is an on-going investigation.

References:

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