HyperNIR: Overcoming the limitations of the heavy atom effect in near infrared luminophores

Harnessing the 'invisible' light

Near infrared (NIR) spectral range lies just outside of the visible range – at its red edge. While the actual boundary is blurred, we often assume that NIR starts at 700 nm and ends at around 1400 nm when it transitions into mid infrared. NIR light has the same properties as visible light and can in principle be used for illumination – the caveat being that we cannot see NIR. This property of NIR opens up a plethora of applications, such as in light-based communications or night vision. NIR falls within the transparency window of biological tissue – a region of spectrum where the molecules present inside living organisms absorb the least light. Thanks to this property, NIR can be used for medical or imaging applications where light is either a part of treatment or allows visualising structures hidden within the tissue. The most down-to-earth medical application of red and NIR light is blood oximetry – an optical method to determine oxygen content in blood.

Making them smaller

Organic light-emitting diodes (OLEDs) are small devices that use organic materials to create light. They are currently used for purposes where miniscule pixel sizes are desired, such as in high definition TV or mobile phones displays. OLEDs are flat, thin, and can be bendable. Now imagine OLEDs producing NIR light that can be tiny and flexible – we can incorporate them into a small plaster. That plaster can then monitor our blood oxygen levels and we wouldn't even notice! This is only one of the many applications NIR OLEDs may have.

TADF – what's all about?

Thermally activated delayed fluorescence (TADF) is a very important luminescent mechanism that has a plethora of applications (Figure 1). This mechanism is related to the properties of the so-called excited states of molecules - states which occur once the molecule gains energy through absorption of light or electrical excitation. The molecule instead of returning to its initial, ground state (S_0) through the slower path via phosphorescence from the triplet (T_1) state, transitions through an upper, singlet state (S_1) , returning to the ground state faster, via fluorescence. The energy difference between S_1 and T_1 , ΔE_{S-T} , is usually expressed in physical units of energy – electronvolts (eV). Typical values for TADF fluorescent dyes are below 200 millielectronvolts (meV).

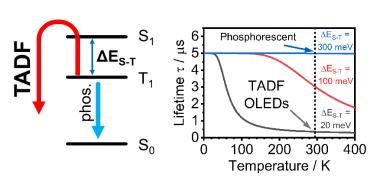


Figure 1. (*left*) Schematic representation of TADF mechanism; (*right*) example of how TADF shortens radiative decay lifetime of a metalorganic emitter from its natural phosphorescence rate at 5 microseconds to 500 nanoseconds at room temperature and with $\Delta E_{ST} = 20$ meV.

What's the advantage of TADF for NIR?

NIR-luminescent materials are strongly affected by the so-called non-radiative decay which is detrimental to their emission properties. Scientists have come up with a term for this effect: the energy gap law. Now imagine a race between two cars: one of them being the radiative decay, the other the non-radiative decay. The faster car is ultimately the one that wins the race. Whichever car wins, it will determine the luminescent properties of the molecule. We would like that the radiative processes win, to make our molecules more luminescent. There are two ways to make this happen: 1) slow down the non-radiative process or 2) speed-up the radiative process. In this project we decided to go with option 2. By using TADF we can achieve an incredible acceleration of the radiative decay that is not possible otherwise. As we are able to significantly speed-up the luminescent processes, the non-radiative processes are outcompeted leading to highly-luminescent molecules.