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## Low-temperature spectroscopic studies of single molecules in 3-D and on 2-D hosts

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## SUMMARY

Spectroscopic studies of fluorescent single molecules in organic condensed matter do not only provide information about the molecule itself, but also about its near environment. By suppression of phonon-induced broadening of spectral lines through cooling to low temperatures, small changes in the spectral lines' position can be uncovered in response to weak variations in local electric fields. These variations can for instance be caused by rearrangements of charges or minute changes in the crystal lattice around the molecule. Therefore, molecules are sensitive sensors for the study of physical phenomena at the nanoscale.

This sensitivity of molecules to subtle changes in their near environment only works when the spectral lines are narrow enough. At best the linewidths reach the absolute minimum, dictated by the excited state's lifetime. It is, however, not a given that every fluorescent molecule in a random organic crystal will have narrow spectral linewidths at low temperature. So far, there are in fact only very few combinations of fluorescent molecules in organic crystals that displayed narrow spectral linewidths. Then, what makes a good combination? As a rule of thumb it is important that the electronic energy levels of the crystal lattice are higher in energy than those of the embedded fluorescent molecules, in order to assure there is no loss of excitations due to transfer of energy. In the case of efficient energy transfer, there will be significant loss of fluorescence from the molecule. Furthermore, the crystal lattice must be stable at low temperature, while also a weak coupling of the fluorescent molecule to lattice vibrations is desired for. Lastly, it is empirically important that the fluorescent molecule and the molecules of the organic crystal are similar in shape and size, such that the fluorescent molecule can be well embedded into the crystal. However, a clear theory that describes what works well and what does not is absent at the moment. Moreover, even though a combination satisfies the above conditions, the crystal can still have far reaching implications on the properties of the fluorescent molecule that it incorporates.

To have more examples of combinations that give rise to narrow linewidths, we have studied two new organic crystals with the embedded fluorescent molecules perylene (Chapter 2) and terylene (Chapter 4). In both cases, the fluorescent molecules show narrow spectral lines at low temperature, whose widths closely reach the absolute limit dictated by the lifetime of the excitation. The measured properties of the molecules are however strongly influenced by the crystal lattice around them. For instance, in Chapter 2 we report that perylene molecules in a dibenzothiophene crystal show a stronger-than-normal fluorescence signal upon strong excitation. At weak excitation perylene's fluorescence displays normal intermittency in the fluorescence signal due to transitions to a non-fluorescent state, namely the triplet state. Through stronger excitation, the time that perylene resides in the triplet state can be shortened by a few orders of magnitude, leading to a higher fluorescence output. Although this effect of reverse intersystem crossing is known, the effect had not been observed

before at liquid-helium temperatures of below 4 K. For terrylene in Chapter 4, we observed that the sensitivity of spectral lines to electric fields is enhanced. This is a consequence of the crystal lattice that surrounds the terrylene molecule and influences the charge distribution within the molecule in the ground state and excited state, and effectively creates a static dipole moment. The induced dipole moment causes terrylene to couple efficiently to electric fields and that makes this combination interesting for mapping electric fields or tracing single charges. To make the process of mapping electric fields as efficient as possible, we fabricated a chip that allowed us to measure for each molecule independently the orientation of the dipole moment, such that not only an electric field magnitude, but also field orientation can be measured.

The two described crystals in Chapter 2 and Chapter 4 possess a three-dimensional structure, but since the discovery of graphene a large number of examples of two-dimensional crystals have been explored. One of them is hexagonal boron nitride (hBN). The electronic and structural properties of hBN makes this material a promising substrate for single fluorescent molecules. We have tested this hypothesis in detail with the fluorescent molecule terrylene, as described in Chapter 5. At low temperature, we observe narrow spectral lines that are about 10-20 times wider than the absolute lifetime limit. In addition, the spectral lines show a spectral diffusion due to coupling to dynamical processes in the near environment of the molecule. Furthermore, we observed that by heating the hBN before deposition of the molecules and therefore cleaning the surface from most organic contamination, the so-called annealing, we can make the spectral lines more stable. Apart from terrylene, we also tested if other molecules could be deposited onto the hBN substrate. We tried this with large graphene molecules, which are normally difficult to incorporate into a three-dimensional crystal. Also for these molecules we observed narrow spectral lines, which gave us direct insight into the vibrational spectrum of these newly-developed molecules.

In the remaining Chapter 3 and Chapter 6 we worked on studies beyond fluorescence, namely on the light emitted from the triplet state, which is usually called phosphorescence. In Chapter 3 we used the crystal described in Chapter 2 to detect the phosphorescence of perylene. In order to be able to detect this very weak signal we created triplet excitations within the crystal itself, so that they could migrate to the limited number of perylene molecules within this crystal. With the phosphorescence spectrum as a result, we could estimate the energy of the triplet state. In Chapter 6 we continued building up an experiment that would allow us to perform a direct excitation from the ground state to the triplet state, where the energy of the laser would be scanned around a bandwidth that is given by the phosphorescence spectrum and its uncertainty. Eventually, this could give us the possibility to study excitations to the triplet state at the single-molecule level, in order to measure the quantum mechanical properties of this state, such as coupling to nuclear spins within the near environment of the molecule. This would make it possible to not only use the molecules as sensors for electric fields, but also magnetic fields.