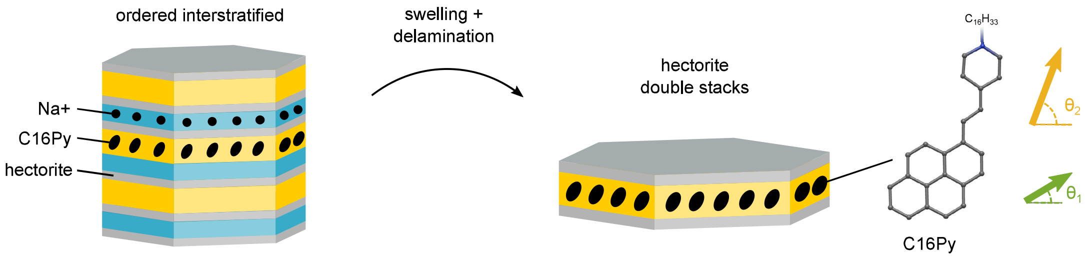

Fig. 3.1.: The sodium ions in the hectorite crystal are partially exchanged with the dye (C16Py), organized as strictly alternating interlayers, called "ordered interstratified" state. The hectorite double stacks are obtained after swelling and delamination [9]. The chemical structure of the C16Py dye is shown on the right with sketched orientations of the two transition dipole moments.

We demonstrate that the hectorite nanosheets can be modelled as a homogeneous dielectric material. The hectorite double stacks with the dye monolayer is described as a single Lorentzian oscillator.

We then present a universal and powerful method to disentangle the orientations of spectrally overlapping transition dipoles in dense dye layers. Parts of this work are published in Nano Letters. We demonstrate that the dye monolayer has two dominating transitions which contribute to the fluorescence spectrum, as sketched by the two transition dipole moments in Figure 3.1. A comprehensive theory model allows an individual orientation determination of both transition dipoles and reveals a long-ranged orientational order on glass substrate. This order becomes even stronger on gold substrates, suggesting a substrate-induced molecule reorientation. Finally, we demonstrate that the fluorescence intensity ratio serves as a probe for the spontaneous emission rate.

Formulate the requirements for the dye: broad spectrum as a feature for broadband coupling with NPoM

3.1 Numerical methods for the optics of layered media

3.1.1 Reflection and transmission at interfaces

We first analyze the reflection and transmission of electromagnetic waves at boundaries between different materials. The wave vectors of incoming, reflected and transmitted waves lie in one plane, therefore we can solve this problem in two dimensions. We choose the xz plane as shown in Figure 3.2. The electric field of a plane wave therefore reads

$$\boldsymbol{E} e^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} = \boldsymbol{E} e^{\mathrm{i}k_x x} e^{\mathrm{i}k_z z} e^{-\mathrm{i}\omega t} \quad . \tag{3.1}$$

With $k_0 = 2\pi/\lambda$ as wave vector in vacuum, we get

$$k_x^2 + k_z^2 = n^2 k_0^2 \quad . \tag{3.2}$$

The electric fields can be decomposed into s- and p-polarization, where s is perpendicular and p is parallel to the plane of incidence. This defines the unit vectors

$$\hat{\boldsymbol{E}}^{(s)} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \hat{\boldsymbol{E}}^{(p)} = \frac{1}{nk_0} \begin{pmatrix} \pm k_z \\ 0 \\ k_x \end{pmatrix} \tag{3.3}$$

with $|\hat{\boldsymbol{E}}^{(s)}|^2 = |\hat{\boldsymbol{E}}^{(p)}|^2 = 1$. The $\pm$ in the x component comes from the definition of the reflected electric field pointing into the opposite x direction. Imposed by the boundary conditions of the electric field defined by Maxwell's equations for nonmagnetic media, one can define reflection and transmission coefficients r_{12} and t_{12} for the electric fields propagating from medium 1 to medium 2

$$r_{12}^{(s)} = \frac{k_{z,1} - k_{z,2}}{k_{z,1} + k_{z,2}} = -r_{21}^{(s)} \tag{3.4}$$

$$t_{12}^{(s)} = \frac{2k_{z,1}}{k_{z,1} + k_{z,2}} = \frac{k_{z,1}}{k_{z,2}} t_{21}^{(s)} \tag{3.5}$$

$$r_{12}^{(p)} = \frac{\varepsilon_2 k_{z,1} - \varepsilon_1 k_{z,2}}{\varepsilon_2 k_{z,1} + \varepsilon_1 k_{z,2}} = -r_{21}^{(p)} \tag{3.6}$$

$$t_{12}^{(p)} = \frac{2\sqrt{\varepsilon_1 \varepsilon_2} k_{z,1}}{\varepsilon_2 k_{z,1} + \varepsilon_1 k_{z,2}} = \frac{k_{z,1}}{k_{z,2}} t_{21}^{(p)} \tag{3.7}$$

Due to the definition of the electric field vectors in Figure 3.2, the signs of $r_{12}^{(s)}$ and $r_{12}^{(p)}$ differ in sign at perpendicular incidence. Here we also gave the reflection coefficients for the reverse propagation direction which we will use later. Note that the x-component does not change at interfaces due to momentum conservation. Hence, k_x is a global constant defined by the incident wave. The propagation direction defines an angle θ with respect to the z axis

$$\theta = \arcsin \frac{k_x}{nk_0} = \arcsin \sqrt{1 - \frac{k_z}{nk_0}} \quad . \tag{3.8}$$

One defines the power reflection coefficient $R_{12} = |r_{12}|^2$ which gives the percentage of the incident power being reflected. In transmission one needs to take the refraction into account. The power transmission coefficient is therefore $T_{12} = \frac{n_2 \cos \theta_2}{n_1 \cos \theta_1} |t_{12}|^2 = \frac{k_{z,2}}{k_{z,1}} |t_{12}|^2$. This ensures energy conservation $T_{12} + R_{12} = 1$.

3.1.2 Transfer matrix

In the general case of a multi-layered system, the electric field in each medium i can be decomposed into waves traveling into left and right direction, with amplitudes $U_i^{(-)}$ and $U_i^{(+)}$

$$\boldsymbol{E}_i^{(s,p)} = \hat{\boldsymbol{E}}^{(s,p)} \left(U_{i,(s,p)}^{-} e^{-\mathrm{i}k_z z} + U_{i,(s,p)}^{+} e^{\mathrm{i}k_z z} \right) e^{\mathrm{i}(k_x x - \omega t)} \tag{3.9}$$

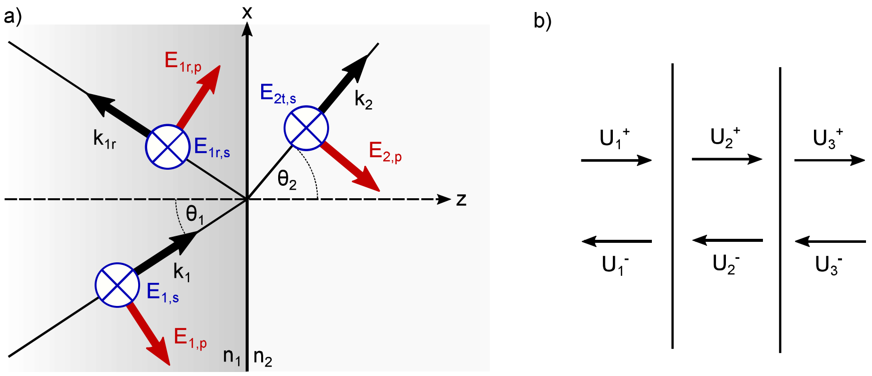

Fig. 3.2.: Reflection and transmission at interfaces **Does reflected p-pol point into opposite direction?**

Since both polarizations can be treated independently, we drop the indices s and p from now on. The amplitudes in neighboring media have the linear relation

$$\begin{pmatrix} U_2^+ \\ U_2^- \end{pmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \cdot \begin{pmatrix} U_1^+ \\ U_1^- \end{pmatrix} = \boldsymbol{M} \begin{pmatrix} U_1^+ \\ U_1^- \end{pmatrix} \tag{3.10}$$

with transfer matrix M, where we decided for the specific case of media 1 and 2. Generally, the propagation through multi-layered media is described by the product of the individual matrices $\boldsymbol{M}_i$ as

$$\boldsymbol{M}_{total} = \boldsymbol{M}_n \cdot \boldsymbol{M}_{n-1} \cdots \boldsymbol{M}_1 \tag{3.11}$$

Consider the case of an incident wave traveling to the right with amplitude U_1^+. The reflected amplitude U_1^- enters on the right side of equation 3.10, but is unknown in the first place. Therefore, we define the scattering matrix $\boldsymbol{S}$ which relates the wave amplitudes propagating to the interface with the ones traveling away from it. The entries of the scattering matrix are the transmission and reflection coefficients we defined earlier:

$$\begin{pmatrix} U_2^+ \\ U_1^- \end{pmatrix} = \begin{pmatrix} t_{12} & r_{21} \\ r_{12} & t_{21} \end{pmatrix} \cdot \begin{pmatrix} U_1^+ \\ U_2^- \end{pmatrix} = \boldsymbol{S} \begin{pmatrix} U_1^+ \\ U_2^- \end{pmatrix} \tag{3.12}$$

The following relations between the entries of $\boldsymbol{M}$ and $\boldsymbol{S}$ allow us to switch between the two representations if $D \neq 0$ and $t_{21} \neq 0$ **(citation Saleh/Teich)**:

$$\boldsymbol{M} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} = \frac{1}{t_{12}} \begin{pmatrix} t_{12}t_{21} - r_{12}r_{21} & r_{21} \\ -r_{12} & 1 \end{pmatrix} \tag{3.13}$$

$$\boldsymbol{S} = \begin{pmatrix} t_{12} & r_{21} \\ r_{12} & t_{21} \end{pmatrix} = \frac{1}{D} \begin{pmatrix} AD - BC & B \\ -C & 1 \end{pmatrix} \tag{3.14}$$

Using our definitions of reflection and transmission coefficients in the last chapter the transfer matrix of an interface reads for both polarizations

$$\boldsymbol{M}_{12} = \frac{1}{t_{21}} \begin{pmatrix} 1 & r_{21} \\ r_{21} & 1 \end{pmatrix} = \frac{1}{2\eta} \begin{pmatrix} 1+\kappa & 1-\kappa \\ 1-\kappa & 1+\kappa \end{pmatrix} \tag{3.15}$$

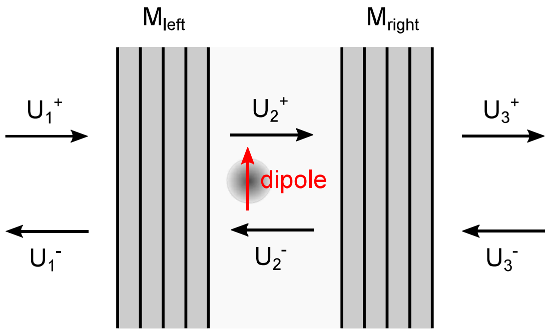

Fig. 3.3: Dipole in multi-layered environment

with $\eta^{(s)} = 1$, $\eta^{(p)} = \sqrt{\varepsilon_2/\varepsilon_1}$ and $\kappa = \eta^2 k_{z,1}/k_{z,2}$. Propagation through media for a distance d imposes a phase on the electric field. We can use the same framework as for interfaces, defining a complex transmission coefficient $t = t_{12} = t_{21} = e^{ik_z d}$. As the propagation direction has already been included in our definition of the electric field 3.9, the the exponent has a positive sign for both transmission coefficients. The reflection coefficient is $r = r_{12} = r_{21} = 0$ during propagation. Therefore, the transfer matrix of propagation in a homogeneous medium with wave vector reads

$$\boldsymbol{M} = \begin{pmatrix} e^{ik_z d} & 0 \\ 0 & e^{-ik_z d} \end{pmatrix} \tag{3.16}$$

Add reflection and transmission coefficient through arbitrary media, for refractive index measurements

3.1.3 Dipoles in multi-layered environments

The transfer matrix formalism allows to calculate the electric field at every position in a multi-layered environment. As a consequence, one can obtain the amplitude of a dipole moment within the system driven by the electric field. In this chapter we will derive a formalism at plane wave excitation from the right side of the system under a certain angle.

Since the propagation of light beams can be reversed, this is equivalent to a dipole emitting into the far field under the same angle. Hence, we can determine the emission pattern of a dipole in a multi-layered environment. The results will be compared with the literature at the end of this chapter. **(how?, only works for planar environments, but there are ways by fourier transform!?)**

The electric field at the position of a dipole is obtained by simplifying an arbitrary multi-layered environment to an effective three layer system as sketched in Figure 3.3. The layers left and right of the dipole are combined in the transfer matrices $\boldsymbol{M}_{\text{left}}$ and $\boldsymbol{M}_{\text{right}}$, including the propagation to and from the dipole. The complex field amplitudes of the left- and right-propagating waves at the position of the dipole are therefore given by U_2^+ and U_2^-. The system is described by

$$\begin{pmatrix} U_3^+ \\ U_3^- \end{pmatrix} = \boldsymbol{M}_{\text{right}} \begin{pmatrix} U_2^+ \\ U_2^- \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} U_2^+ \\ U_2^- \end{pmatrix} = \boldsymbol{M}_{\text{left}} \begin{pmatrix} U_1^+ \\ U_1^- \end{pmatrix} \quad . \tag{3.17}$$

Imagine a plane wave entering the the system from the right (medium 3). Medium 1 will only have an outgoing wave to the left, i.e., $U_1^+ = 0$. Furthermore, we choose $U_1^- = 1$. This gives the relations **(M now includes propagation!)**

$$\begin{pmatrix} U_2^+ \\ U_2^- \end{pmatrix} = \boldsymbol{M}_{\text{left}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{t_{21}} \begin{pmatrix} t_{12}t_{21} - r_{12}r_{21} & r_{21} \\ -r_{12} & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3.18}$$

$$= \frac{1}{t_{21}} \begin{pmatrix} r_{21} \\ 1 \end{pmatrix} \tag{3.19}$$

$$\begin{pmatrix} U_3^+ \\ U_3^- \end{pmatrix} = \boldsymbol{M}_{\text{right}} \begin{pmatrix} U_2^+ \\ U_2^- \end{pmatrix} = \frac{1}{t_{32}} \begin{pmatrix} t_{23}t_{32} - r_{23}r_{32} & r_{32} \\ -r_{23} & 1 \end{pmatrix} \cdot \frac{1}{t_{21}} \begin{pmatrix} r_{21} \\ 1 \end{pmatrix} \tag{3.20}$$

$$= \frac{1}{t_{21}t_{32}} \begin{pmatrix} (t_{23}t_{32} - r_{23}r_{32})r_{21} + r_{32} \\ -r_{23}r_{21} + 1 \end{pmatrix} \tag{3.21}$$

The electric fields normalized to the incident amplitude U_3^- at the position of the dipole are **(spectroscopy script has r_{12} instead of r_{21}. This is corrected here, marked in red, seems to only make difference in environment with absorption)**

$$E_2^+ = \frac{U_2^+}{U_3^-} = \frac{r_{21}}{t_{21}} \cdot \frac{t_{21}t_{32}}{1 - r_{23}r_{21}} = \frac{r_{21}t_{32}}{1 - r_{23}r_{21}} \tag{3.22}$$

$$E_2^- = \frac{U_2^-}{U_3^-} = \frac{1}{t_{21}} \cdot \frac{t_{21}t_{32}}{1 - r_{23}r_{21}} = \frac{t_{32}}{1 - r_{23}r_{21}} \tag{3.23}$$

The electric field for an illumination from the left can easily be obtained by swapping the indices 1 and 3 and the propagation direction

$$E_2^- = \frac{U_2^+}{U_3^-} = \frac{r_{23}t_{12}}{1 - r_{21}r_{23}} \tag{3.24}$$

$$E_2^+ = \frac{U_2^-}{U_3^-} = \frac{t_{12}}{1 - r_{21}r_{23}} \tag{3.25}$$

We define a Finesse parameter

$$F^{(s,p)} = \frac{1}{1 - r_{23}^{(s,p)} r_{21}{}^{(s,p)}} \tag{3.26}$$

For incident wave propagating to the left ($\leftarrow$) and right ($\rightarrow$) one obtains an electric field at the position of the dipole as superposition of left- and right traveling waves

$$\boldsymbol{E}_{\leftarrow} = \begin{pmatrix} -F^{(p)}t_{32}^{(p)}\left(1 - r_{21}^{(p)}\right)\frac{k_{z,1}}{k_2} \\ F^{(s)}t_{32}^{(s)}\left(1 + r_{21}^{(s)}\right) \\ F^{(p)}t_{32}^{(p)}\left(1 + r_{21}^{(p)}\right)\frac{k_x}{k_2} \end{pmatrix} \quad \text{and} \quad \boldsymbol{E}_{\rightarrow} = \begin{pmatrix} F^{(p)}t_{12}^{(p)}\left(1 - r_{23}^{(p)}\right)\frac{k_{z,1}}{k_2} \\ F^{(s)}t_{12}^{(s)}\left(1 + r_{23}^{(s)}\right) \\ F^{(p)}t_{12}^{(p)}\left(1 + r_{23}^{(p)}\right)\frac{k_x}{k_2} \end{pmatrix} \tag{3.27}$$

In the x component the difference and not the sum of left- and right-propagating enters, since the x component of the p-polarized wave flips by the definition in Figure 3.2. The global minus in the x-component of $\boldsymbol{E}_{\leftarrow}$ comes from the propagation to the left.