SUPPORTING INFORMATION

Self-interference of exciton emission in organic single crystals visualized by energy-momentum spectroscopy

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MOMENTUM-FILTERING OF THE EMISSION SPECTRUM OF A SINGLE 3TBT CRYSTAL

Figure S1: Characterisation of the emission properties of a very thin crystal. (a) Widefield image of the emission. (b) Back focal plane image of the emission upon excitation of the crystal at the red marked position in (a). We observe two defined radiation lobes in positive and negative $k_y$-direction indicating (the onset of) active waveguiding of the emission along the crystal as discussed in our former study [1]. (c) Corresponding energy-momentum spectrum (explanation see manuscript), which displays the emission spectra for each available value $k_y$. We introduce a parameter $a$ and integrate the energy-momentum spectra along the momentum axis in the range $|k_y|/k_0 < a$. (d) Resulting spectra for $a = 0.5$ to $a = 1.4$ in steps of 0.1. The spectra are normalized to 1 and smoothed for the presentation. For $a < 0.5$ a constant spectrum is detected which features a distorted vibronic progression with a mean energy difference of about 0.17 eV. Increasing $a$, i.e. taking also emission with higher radiation angles into account, a distinct reduction of the high energy emission peak at about 2.3 eV is observed. In other words, the shape of the detected emission spectra is depending strongly on the direction of emission. This behavior we attribute to a non-trivial local density of optical states for the emitting aggregates inside the crystal. In the spectral range of the high energy emission peak the emission spectrum overlaps with the absorption of the crystal [2, 1] (see also manuscript figure 1b). The monotonic reduction of the high energy emission peak with increasing radiation angle we mainly attribute to an increased amount of reabsorption. The spectrum obtained for $a < 0.5$ we thus attribute to the intrinsic properties of the 3TBT molecules. In this case, the spectrum is assumed to follow $|\mu|^2 \omega^3$, where $\mu$ is the transition dipole moment, including Franck-Condon factor to account for coupling to vibrational modes, and $\omega^3$ is the trivial density of states proportionality.
EMISSION MAPS AND BACK FOCAL PLANE IMAGE

Figure S2: (a) Widefield image of the emission of the 3TBT crystal shown in figure 2 in the manuscript. (b) Emission map of the same crystal area when excited with a diffraction limited laser-spot. We observe strong emission at the excitation spot and weak emission spatially separated from the excitation spot. The latter we attribute to leakage radiation from propagating substrate modes. (c) Corresponding back focal plane image of the emission upon confocal excitation, see (b).
The simulation considers a three layer system, where $n_1 = 1.5$ represents the substrate and $n_3 = 1.0$ is considered as air. The crystal medium in the middle is modelled by an anisotropic (uniaxial) and complex valued refractive index with components $\tilde{n}_{2x} = n_{2x} + i n'_{2x}$ and $\tilde{n}_{2yz} = n_{2yz} + i n'_{2yz}$. The wavevector in vacuum, substrate and air we denote with $k_0$, $k_1$ and $k_3$, respectively. The in-plane and out-of-plane components are described by $k_{iy}$ and $k_{iz}$ ($i = 1, 3$). The wavevector in the crystal medium 2 is complex with out-of-plane component:

$$\tilde{k}_{2z} = k_{2z} + ik'_{2z}$$

(1)

The calculation of the radiation characteristics is based on the reciprocity theorem like in references [3, 4]. We expand the formalism to complex valued anisotropic refractive indizes of the emitting medium 2. Starting with a given in plane wavevector magnitude in medium 1 (side of detection) $k_{1y}$ we calculate the z-component of the complex wavevector $\tilde{k}_{2z}$ in the anisotropic medium 2 [5, 6]:

perpendicular polarized: $\tilde{k}_{2z} = \frac{\sqrt{(n_{2x}^2 + n'_{2x}^2)k_0^2 - k_{1y}^2}}{\sqrt{n_{2x}^2 + n'_{2x}^2}}(n_{2x} + in'_{2x}),$

(2)

parallel polarized: $\tilde{k}_{2z} = \frac{\sqrt{(n_{2yz}^2 + n'_{2yz}^2)k_0^2 - k_{1y}^2}}{\sqrt{n_{2yz}^2 + n'_{2yz}^2}}(n_{2yz} + in'_{2yz}).$

This allows to calculate the cosine of the propagation angle $\theta_2$ in the crystal medium 2:

perpendicular polarized: $\cos(\theta_2) = k_{2z}/(n_{2x} \cdot k_0),$

parallel polarized: $\cos(\theta_2) = k_{2z}/(n_{2yz} \cdot k_0).$
The Fresnel coefficients for reflection \( r_{ij}^{p,s} \) and transmission \( t_{ij}^{p,s} \) between layer \( i \) and \( j \) for parallel (p) and perpendicular (s) polarization are given by:

\[
\begin{align*}
  r_{21}^{p} &= \frac{n_1^2 k_{2z} - n_2^2}{n_2^2 k_{1z} + n_1^2 k_{2z}}, & r_{21}^{s} &= \frac{k_{2z} - k_{1z}}{k_{2z} + k_{1z}}, \\
  r_{23}^{p} &= \frac{n_3^2 k_{2z} - n_2^2}{n_2^2 k_{3z} + n_3^2 k_{2z}}, & r_{23}^{s} &= \frac{k_{2z} - k_{3z}}{k_{2z} + k_{3z}}, \\
  t_{12}^{p} &= \frac{2n_1 k_{2z}}{n_2^2 k_{1z} + n_1^2 k_{2z}}, & t_{12}^{s} &= \frac{2k_{1z}}{k_{1z} + k_{2z}}.
\end{align*}
\]

We define the shortcut \( \gamma \) as follows:

\[
\gamma = \left( \frac{\mu(\omega)^2 \omega^3}{3e^3 \pi \epsilon_0} \right) \frac{n_1 k_1}{8\pi k_1^2 k_{1z}},
\]

where \( \mu \) is the transition dipole moment of the emitting aggregates, \( \omega \) the angular frequency, \( c \) the speed of light in vacuum and \( \epsilon_0 \) the vacuum permittivity. The rate of electric dipole transitions per \( \partial \omega \) and \( \partial k_{||} \) for the case of perpendicular polarization is calculated as follows:

\[
\Gamma_\omega^p(\omega, k_{||}) = \gamma \left| \frac{t_{12}^p e^{i k_{2z} d_1 - k_{1z} d_1 / \cos^2(\theta_2)}}{1 - r_{23}^p r_{21}^p e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)}} \left( 1 + r_{23}^s e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)} \right) \right|^2.
\]

For parallel polarization we get:

\[
\Gamma_\omega^y(\omega, k_{||}) = \gamma \left| \frac{t_{12}^p e^{i k_{2z} d_1 - k_{1z} d_1 / \cos^2(\theta_2)}}{1 - r_{23}^p r_{21}^p e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)} - \frac{k_{2z}}{n_2 k_0} \left( 1 - r_{23}^p e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)} \right) \right|^2,
\]

\[
\Gamma_\omega^z(\omega, k_{||}) = \gamma \left| \frac{t_{12}^p e^{i k_{2z} d_1 - k_{1z} d_1 / \cos^2(\theta_2)}}{1 - r_{23}^p r_{21}^p e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)} - \frac{k_{2z}}{n_2 k_0} \left( 1 + r_{23}^p e^{2i k_{2z} d_2 - 2k_{1z} d_2 / \cos^2(\theta_2)} \right) \right|^2.
\]

We like to point out that the imaginary part \( k_{2z} \) has to enter the equations multiplied with the factor \( 1 / \cos^2(\theta_2) \) because the waves are only attenuated in medium 2. In contrast the phase, represented by the real part \( k_{2z} \), also differs outside medium 2 between different light pathways due to the spatially separated transitions to medium 1. To transfer from the energy-dependent element \( \partial k_{||} \) to the constant pixel-size of our spectrometer CCD we weight equations 6, 7 and 8 with \( \omega^2 \) to get a quantity proportional to the detected counts of the CCD pixels.
Figure S4: Energy-momentum spectrum characteristics for three different 3TBT single crystals of different width and height (increasing from top to bottom). (a-c) Real space emission maps for widefield (left) and confocal excitation (right). (d-f) Experimental energy-momentum spectra for horizontal polarizer orientation (x-direction, equals molecular orientation in single crystal). (g-i) Corresponding simulations using the refractive index and x-oriented emitter ensemble as discussed in the manuscript. The crystal height was fitted to 1020 nm for the top crystal (a,d,g) and to 1800 nm for the middle crystal (b,e,h). The bottom crystal (c,f,i) is 3300 nm in height (measured with atomic force microscope, see manuscript figure 2). The increasing heights from top to bottom are consistent with the increasing width, because these dimensions have been shown to be proportional [2].
Figure S5: (a-c) Real space emission maps for widefield (left) and confocal excitation (right) for the three different 3TBT crystals considered in SI figure S4. (d-f) Corresponding intensity profiles (blue crosses) along the y-direction (white arrow in figure S5a-c, white area is taken into account) are fitted with a central gaussian (green, dashed) and an effective exponential decay (red, solid) so that the superposition (black) matches the experimental profile. The full width at half maximum of the central gaussian is similar (0.6-0.8 μm) in all cases. The 1/e-decay length of the exponential is clearly increasing from left (1.2 μm), middle (1.8 μm) to right (3.5 μm). The corresponding heights of the crystals are 1020 nm, 1800 nm and 3300 nm (see SI figure S4). This is interpreted as an increasing effective propagation length of the substrate modes for increasing crystal thickness. (g-i) Calculated (normalized) k-space radiation of a single x-oriented emitter in 1 nm height of a 3TBT layer of 1020 nm, 1800 nm and 3300 nm thickness at 2.16 eV (blue, refractive index used is \( \tilde{n} \)). The substrate modes are numbered with decreasing |k_y|. We calculate the fwhm of each simulated substrate mode and deduce a theoretical propagation length according to \( l_{\text{prop}} = 1/(\text{fwhm} \cdot k_0) \) (see table at bottom). In average the calculated values fit very well to our effective experimental value from d-f. In this study we are not able to detect the properties of single substrate modes. The exponentially distributed ensemble (grey, dashed, refractive index used is \( \tilde{n} \)) shows a broadened width in k-space.
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