Resolving Anisotropic Strong Coupling Effects in Metal-Organic Hybrid Samples

M. Rödel[1], J. Kim[2], M. Stolte[2], L. N. Philipp[3], M. Lehmann[2], F. Würthner[2], R. Mitric[3] and J. Pflaum[1,4]

[1]*Experimental Physics VI, University of Würzburg, 97074 Würzburg, Germany*

[2]*Institut für Organische Chemie and Center for Nanosystems Chemistry, University of Würzburg, 97074 Würzburg, Germany*

[3] *Institut für Physikalische und Theoretische Chemie, University of Würzburg, 97074 Würzburg, Germany*

[4] *Bavarian Center for Applied Energy Research, 97074 Würzburg, Germany*

maximilian.roedel@uni-wuerzburg.de

Coupled light-matter states hold great promises in manipulating physical properties of hybrid materials and in unlocking new functionalities for opto-electronic device applications. Here, we investigate such excited states of hybrid character, called plexcitons, which originate by the interaction of excitons in ordered organic semiconductors and surface plasmons in thin metallic layers [1]. We prepared oriented liquid crystalline J-type aggregates of perylene bisimides (PBI 3, para) [2] on top of silver thin films by off-centred spin coating. Their emerging spatially anisotropic optical behaviour was analysed by means of a Kretschmann-setup probing the absorption and reflection of the samples as function of polar and azimuthal angle. The long-range ordered alignment of the helical PBI strands resulted in a preferred lateral orientation of their molecular transition dipole moments leading to highly anisotropic optical properties, as illustrated in figure 1a). The blue arrow indicates the orientation of the aggregates effective transition dipole moment μ_{eff}. Taking the wave vector of the incident light, k_x, and thus, the propagation direction of the excited plasmons into account, the resulting coupling V between excitonic and plasmonic state becomes angular dependent, as described by $V \propto \vec{\mu} \cdot \vec{E}(k)$. Accordingly, the weakest coupling is expected for parallel and the strongest coupling for perpendicular alignment of μ_{eff} and k_x, which we were able to confirm by the measured 2D dispersions and their anti-crossing splittings of almost 0 meV for the case of $\mu_{eff} \perp k_x$ and the gradually increase to the maximum coupling strength of 27 meV for $\mu_{eff} \| k_x$,. The dispersion curves at these two extreme configurations are displayed in figure 1b) measured at the anti-crossing of the PBI excitonic state at 1.93 eV. Complementary investigations on the photoluminescence of such coupled metal-organic hybrid materials provide insights in the dynamic characteristics of the excitations, in particular, their complex relaxation pathways and transport. In case of our PBI/silver stacks, this leads to interesting variations of the Stokes shifts as well as of the diffusion of excitons upon variation of the azimuthal angle, correlated to the anisotropic alignment of the PBI strands. Understanding these relations between directionality and anisotropic optical properties enables the implementation of such metal-organic hybrid structures in future opto-electronic devices with e.g. steered direction of energy transport.

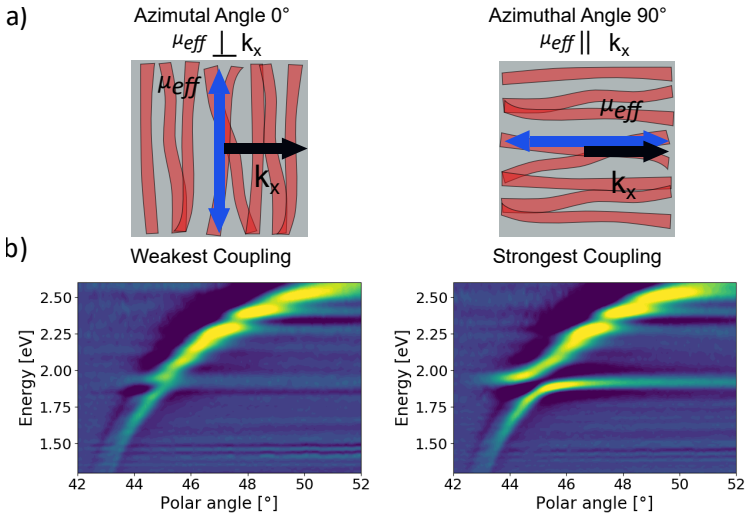

Fig. 1. a) Schematic of the lateral arrangement of ordered molecular PBI strands and their effective transition dipole moment, μ_{eff}, with respect to the wavevector of the propagating plasmons, k_x, for the two extreme configurations of perpendicular (left side) and parallel (right side) orientation. b) Plexciton dispersion spectra in case for the weakest coupling (left side) and the strongest possible coupling (right side).

References

[1] Maximilian Rödel et al., J. Phys. Chem. C 2022, 126(8), 4163-4171.

[2] Stefanie Herbst et al., Nat. Commun. 2018, 9(1), 2646-2654.