

The Idea

In coupled organic-inorganic nanostructures (COINs), inorganic nanoparticles are cross-linked with organic semiconductors (OSCs) and ordered films can be obtained. By utilization of resonant energy levels between the nanocrystals (NC) and the OSC, charge

carrier transport can take place.¹

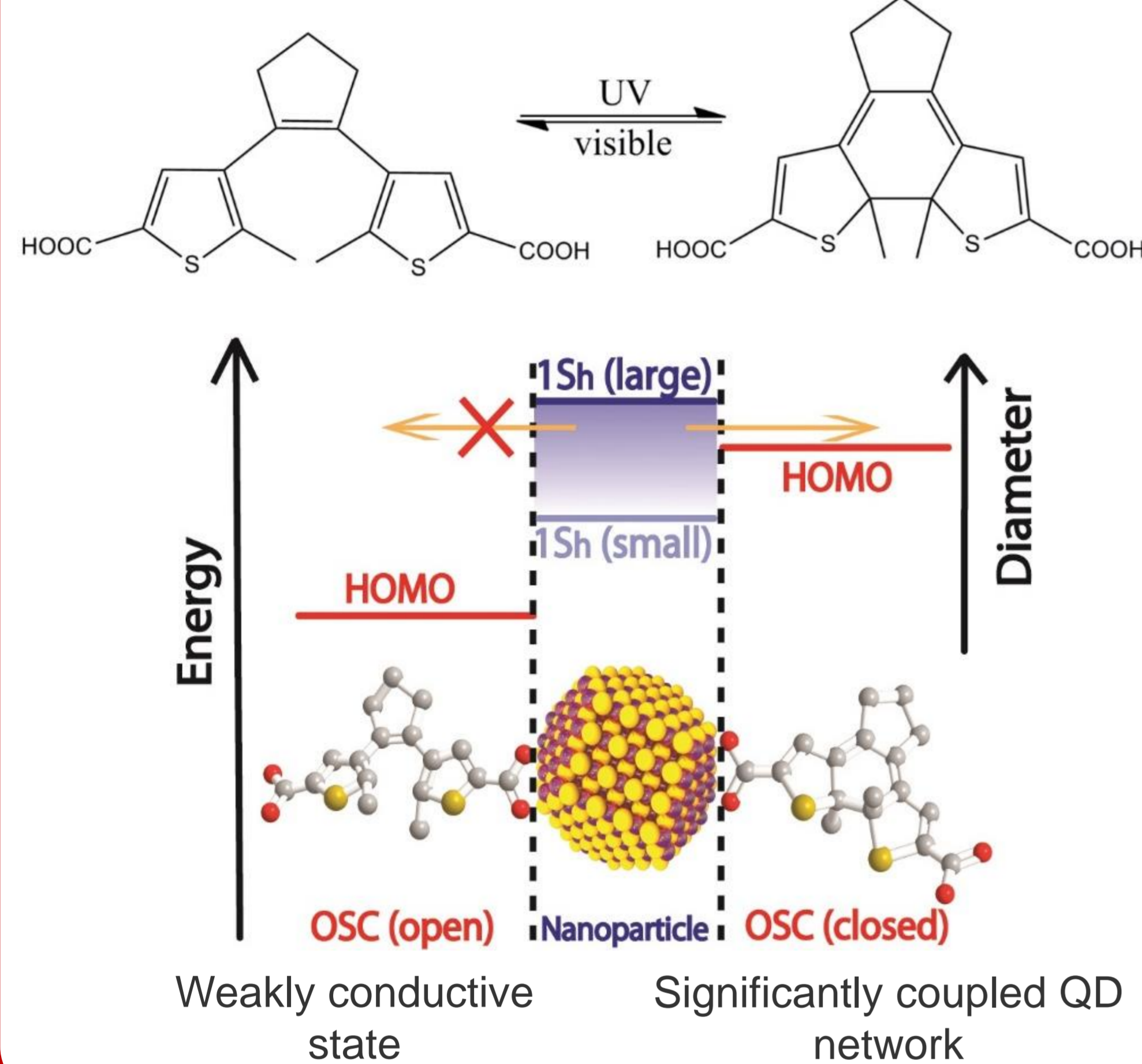
With photochromic molecules as OSC, a switching between two different sets of frontier orbital energy levels can be achieved by light absorption (photo-isomerization) and, thus, charge carrier transport in the COIN is expected to be altered. When implemented in functional

devices, as e.g. field-effect transistors (FETs) or memories, this effect should be optically controllable.

In this work, we investigate the potential of the photochromic molecule 1,2-Bis(5'-carboxy-2'-methylthien-3'-yl)-cyclopentene (DTCP) as photochromic linker to cross-link PbS NC.²

The Ligand: DTCP

We use the photochromic molecule 1,2-Bis(5'-carboxy-2'-methylthien-3'-yl)-cyclopentene (DTCP)³ to cross-link PbS quantum dots (QD) assembled into thin films.

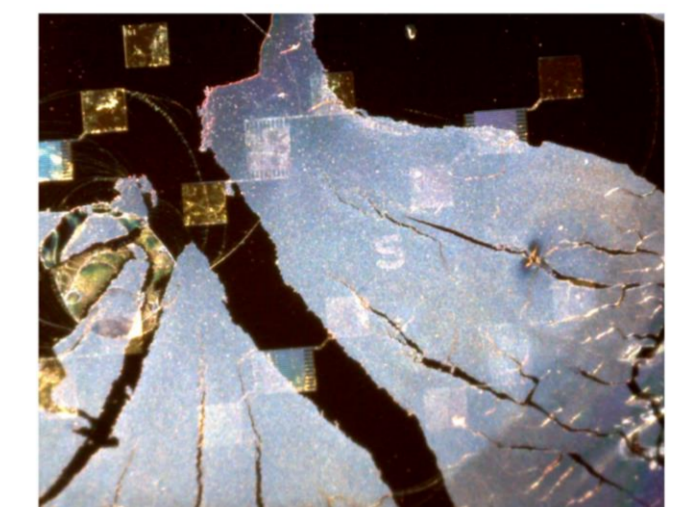


Ligand exchange: Liquid/air exchange

Ligand exchange with DTCP and assembly into superlattices of PbS QDs makes use of a Langmuir-type process of self-assembly at the liquid/air interface.

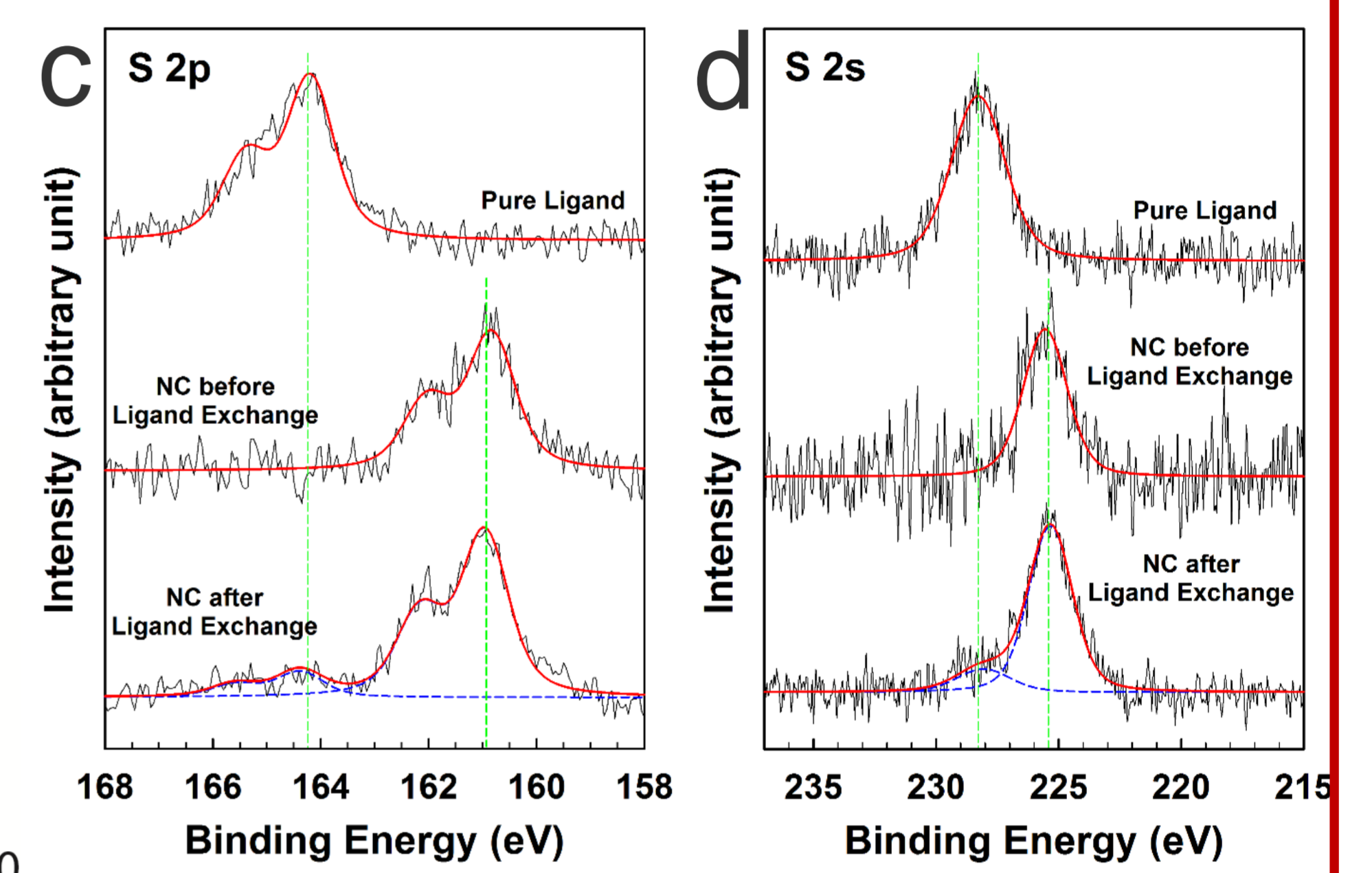
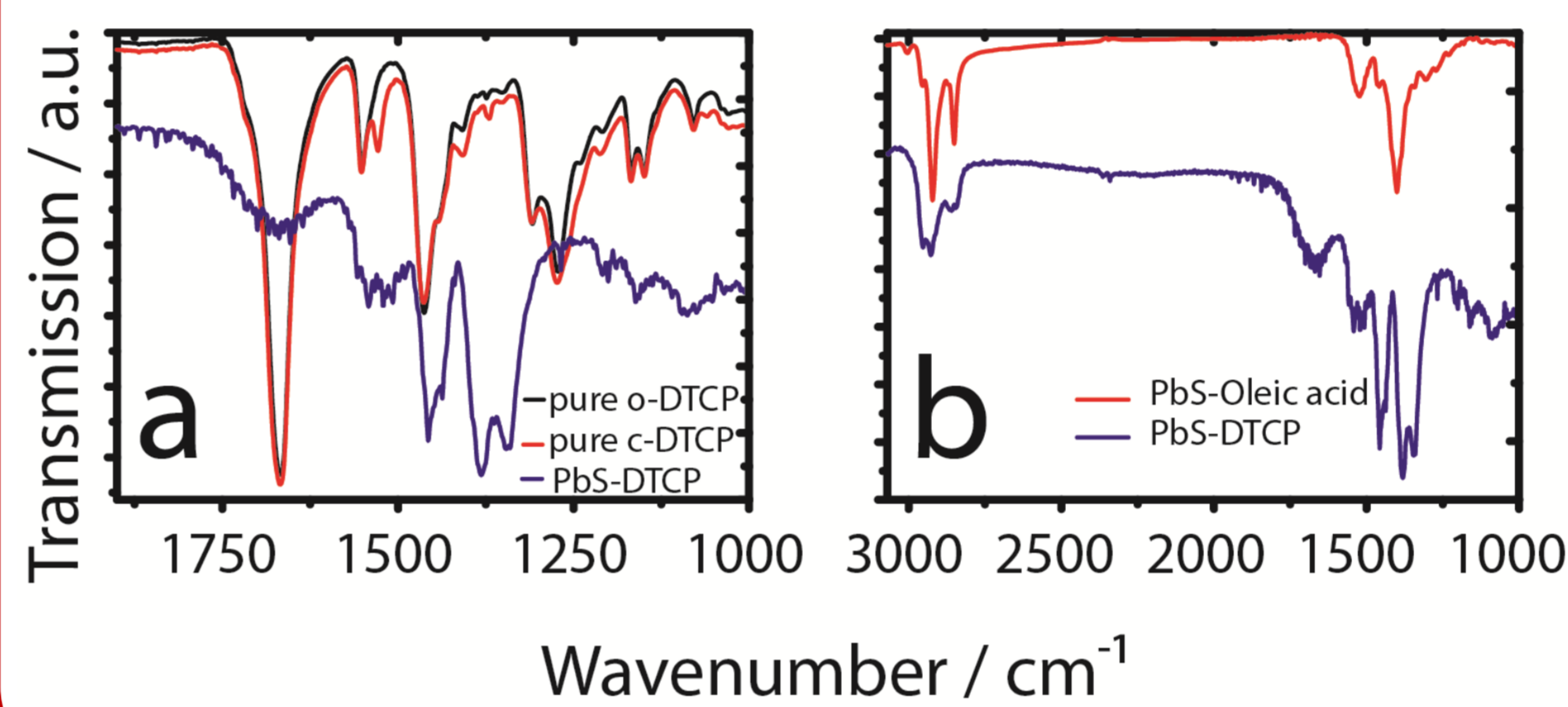
In a homemade reaction chamber, a slanted commercially available FET substrate is covered with acetonitrile and PbS QD are dispersed on top of it. Dissolved DTCP is injected into the subphase and the resulting ligand-exchanged film is transferred onto the substrate.

Photograph of a coated FET substrate



Verification of ligand exchange

with FTIR and XPS. FTIR spectra of **a)** the pure o-DTCP (black) and the pure c-DTCP (red) and of DTCP-treated PbS NC (blue), **b)** of PbS NC before (capped with oleic acid, red) and after treatment with o-DTCP (blue). XPS spectra of **c)** S 2p and **d)** S 2s region, each of pure o-DTCP, pure PbS NC and after ligand exchange.



XPS data courtesy of M. Samadi Khoshkhoo, University of Tübingen

Transport Properties

The films exhibit near-Ohmic behavior in the low field regime with typical conductivities on the order of 1 $\mu\text{S}/\text{cm}$.

Gradual Channel Approximation

The charge carrier mobilities, μ_{lin} , are calculated according to the gradual channel approximation

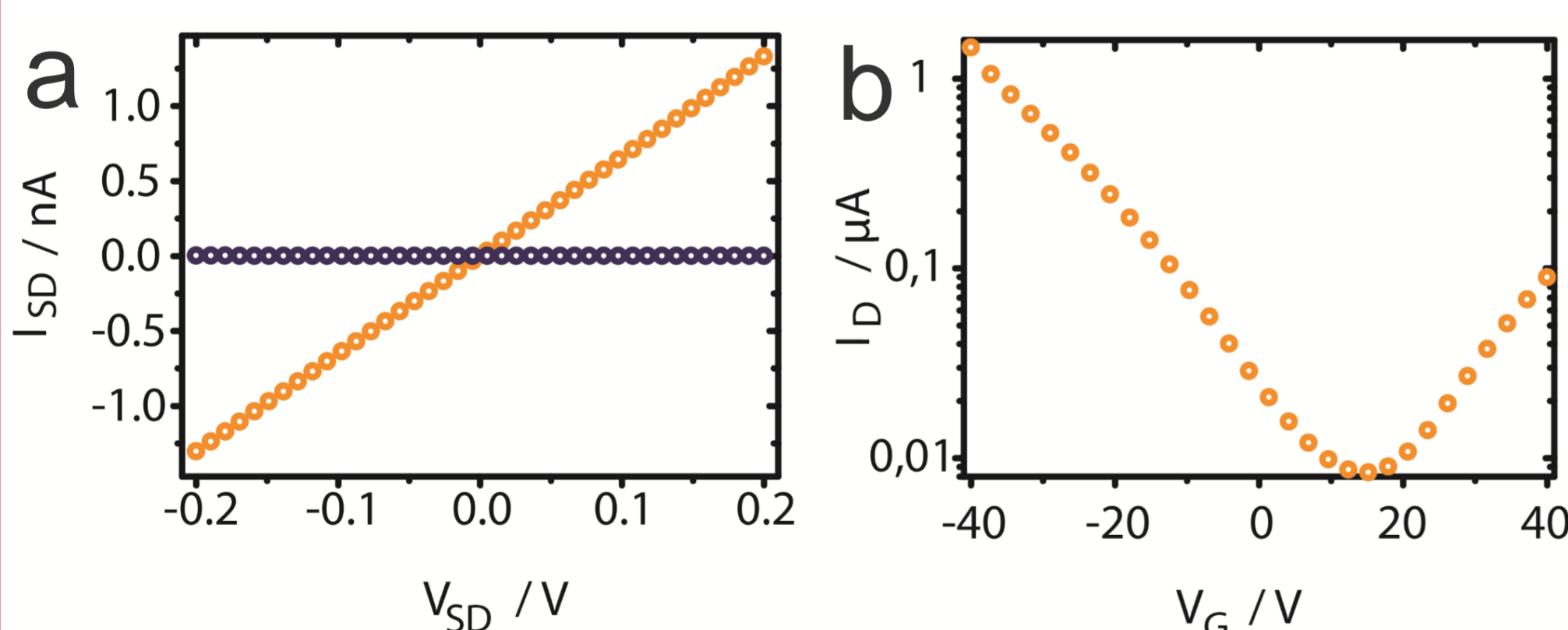
$$\frac{\partial I_{DS}}{\partial V_{GS}} \Big|_{V_{DS}} = \frac{WC_{OX}V_{DS}}{L} \mu_{lin}$$

W: channel width

L: channel length

C_{OX} : capacitance per unit area of gate oxide.

We obtain hole and electron mobilities on the order of $10^{-4} \frac{\text{cm}^2}{\text{Vs}}$ and $10^{-5} \frac{\text{cm}^2}{\text{Vs}}$, respectively.



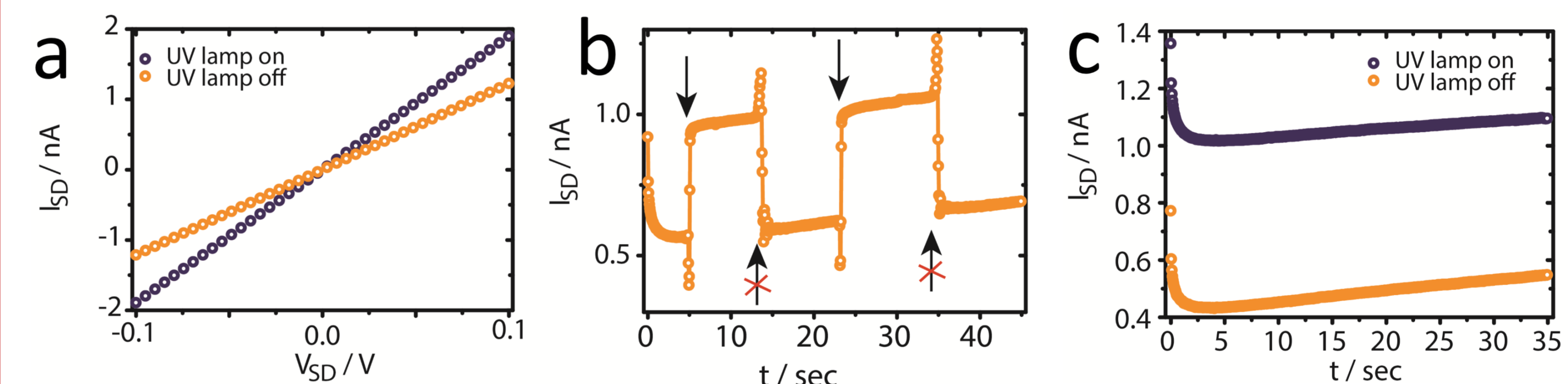
a) Low-field, two-point probe I/V characteristics of a typical PbS-DTCP film (orange) at $V_G = 0$ V. The leakage current via the gate electrode is displayed in blue. **b)** Transconductance of the same device under a constant source-drain bias of +5 V.

Conclusion

We have fabricated nanostructured thin films of PbS QD cross-linked with the photochromic OSC 1,2-Bis(5'-carboxy-2'-methylthien-3'-yl)-cyclopentene. The films exhibit near-Ohmic behavior, and transport measurements in an FET set-up reveal ambipolar behavior. We find a pronounced photoconductance with rapid and reversible photo-response. The hybrid film is expected to be photoswitchable, however, this is hindered in the thin film. A weaker chemical bonding between the QD and the OSC can solve this problem.

Photoconductance

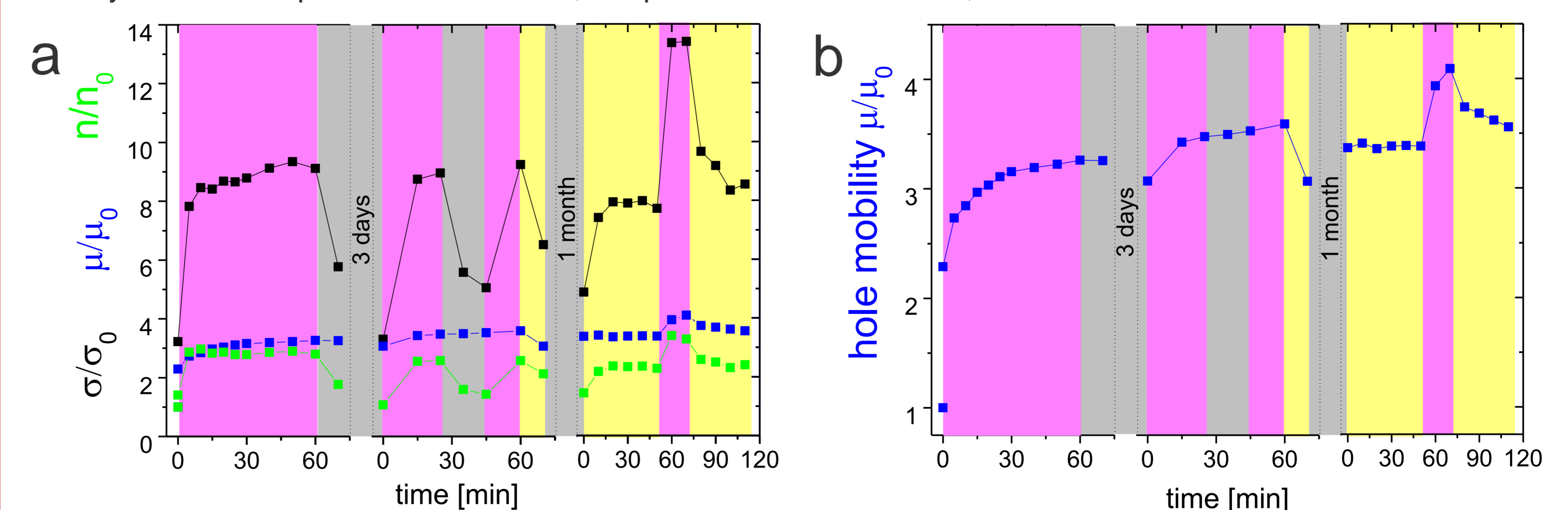
A photoconductance effect of a DTCP-PbS film is observed upon excitation by a 4 W UV-lamp. The conductivity in the low-field regime is found to increase by 50-100 % compared to measurements in the dark. Time dependent measurements show a reversible photoconductance effect with switching times of < 1 s.



a) Low-field, two-point probe I/V characteristics of a typical PbS-DTCP film at $V_G = 0$ V in the dark (orange) and under UV illumination (blue). **b)** Time-dependent two-point probe current measurement at a constant voltage of +1 V of a similar film. Black arrows: beginning of exposure to UV light, crossed arrows: end of an UV exposure period. **c)** Cf. **b)** but under constant UV illumination (blue) or in constant darkness (orange).

Photoswitchability

Carrier mobilities are unaffected by UV irradiation indicating that switching of DTCP is hindered in the hybrid film. By establishing a weaker bound OSC-QD linkage (use of esterificated DTCP) a switching is observable: the hole mobility increases upon UV illumination, keeps constant in the dark, decreases under Vis irradiation.



a) Time-dependent measurements of a DTCP-PbS film with DTCP-diester coating. **b)** Zoom in to the hole mobilities. Black: electrical conductivity σ , blue: hole mobility μ , green: hole concentration n . Violet box: irradiation with UV, grey box: in the dark, yellow box: irradiation with Vis.

References

- [1] M. Scheele, W. Bruetting, F. Schreiber, *Phys. Chem. Chem. Phys.* **2015**, *17*, 97–111.
- [2] C. Schedel, R. Thalwitzer, M. Samadi Khoshkhoo, M. Scheele, *Z. Phys. Chem.* **2017**, *231*(1), 135–146.
- [3] L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg, B. L. Feringa, *Eur. J. Org. Chem.* **2003**, 155–166.