

Direct photo alignment of tetracene via light-directed molecular self-assembly (LDSA)

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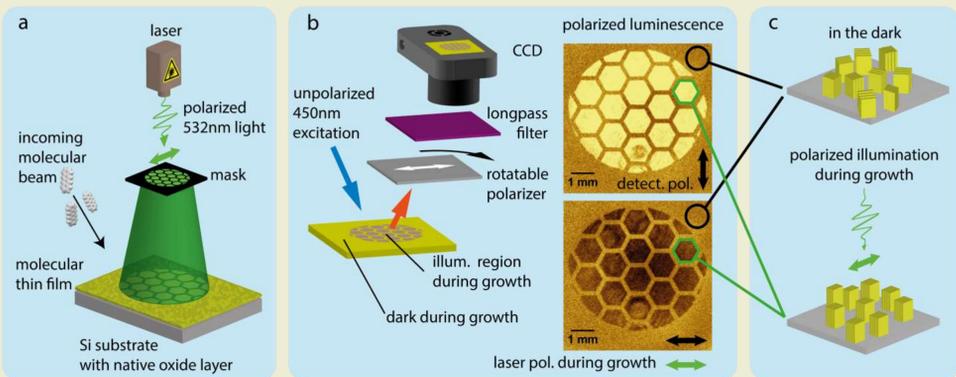
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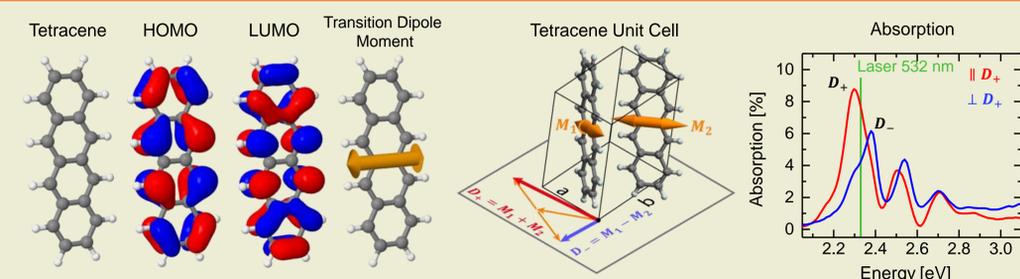


Direct Photoalignment



In order to tailor the formation of organic thin films with enhanced functionality there is a need to establish additional ways to control molecular self-assembly during organic thin film growth. We introduce **light-directed molecular self-assembly (LDSA)** as a novel method to fabricate anisotropic and patterned organic molecular thin films. [1] We employ laser illumination (532nm, ~5W/cm²), matching the molecular absorption band of tetracene (C₁₈H₁₂), during thin film growth to photo lithographically imprint patterns and azimuthally align molecular crystallites. Films produced by LDSA feature linearly polarized photoluminescence and consist of azimuthally aligned molecular crystal grains, even when grown on amorphous substrates such as SiO_x.

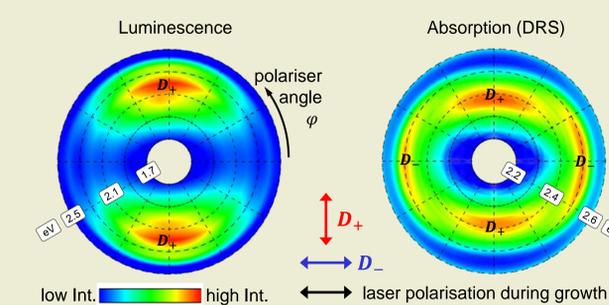
Determining Alignment by Optical Methods



By applying LDSA during tetracene growth on SiO_x (Si substrate with native oxide layer), we demonstrate its capability to induce optical anisotropy and preferential orientations of molecular crystal grains in polycrystalline soft matter thin films. The principal optical transition dipole moment of tetracene (between HOMO and LUMO) is aligned with the short axis of the molecule. [2] Due to the herringbone crystal structure of tetracene with two molecules per unit cell, Davydov splitting leads to a lowest optical transition that is aligned almost parallel to the a-axis of the molecular unit cell.

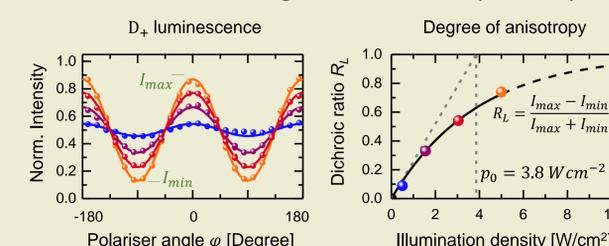
In conventional organic thin film growth the individual crystal grains in polycrystalline thin films are randomly oriented leading to isotropic optical properties parallel to the substrate surface.

Probing the anisotropic optical properties of an LDSA grown film, we can clearly distinguish the lower D₊ and higher D₋ Davydov transition based on their energetic



position and their orientation with respect to the polarization direction of the illumination laser during growth. Spectrally narrow and polarized laser illumination is applied to enhance the formation of crystallites that are oriented such that they absorb less laser light (D₊ ⊥ laser polarization).

The resulting photoalignment is visible in the polarization resolved luminescence signal, where the D₊ shows a 180° symmetry. Using polarization selective differential reflectance spectroscopy [3], we are additionally able to also probe the orientation of the D₋ transition and again find a 180° symmetry.



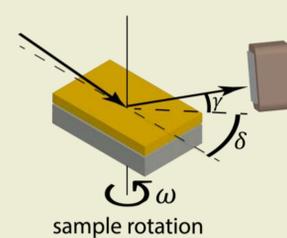
Varying the illumination intensity during thin film growth directly influences the degree of anisotropy following approximately:

$$R_L(p_{laser}) = 1 - e^{-\frac{p_{laser}}{p_0}}$$

Aligned Crystal Grains

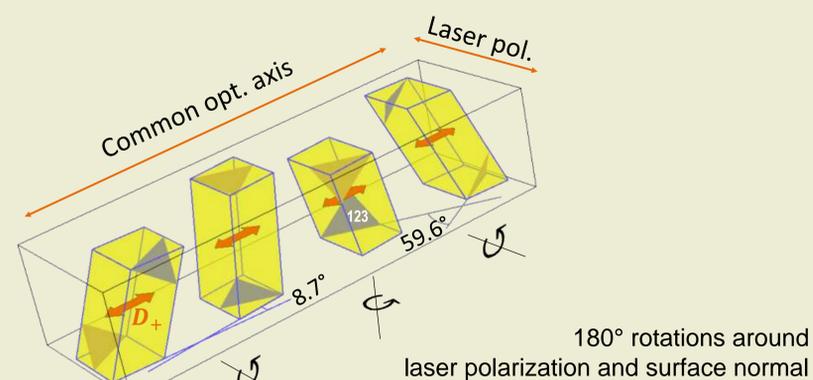
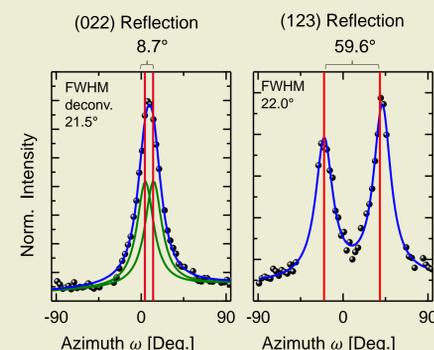
Using grazing incidence x-ray diffraction to monitor the azimuthal intensity distribution of certain tetracene Bragg reflections, we reconstruct the azimuthal orientation of tetracene crystallites.

While the crystallites are randomly distributed in samples grown in the dark (a structure known as 2d powder), we find 4 preferential unit cell orientations for films that were grown under laser illumination.

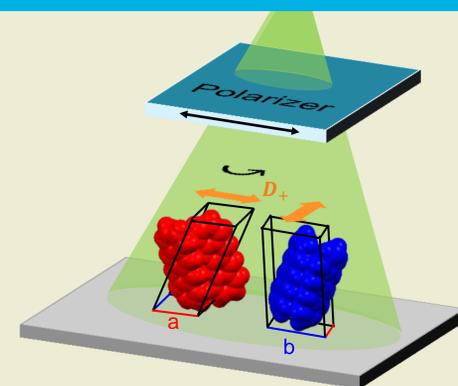
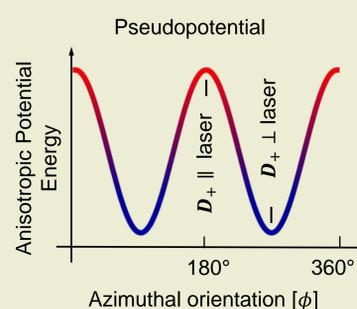


In the LDSA grown film all crystallites are azimuthally aligned such that they share a common D₊ (orientation of the optical transition dipole moment in the unit cell) direction.

Furthermore, we find that the D₊ - axis of the aligned crystallites is oriented perpendicular to the polarization direction of the laser that was illuminating the sample during growth.



Working Principle of LDSA



We propose a mechanism based on opto-thermal re-alignment to explain the observed effect. Crystallites that are oriented such that their D₊ axis (almost equivalent to the a-axis of the molecular unit cell) is aligned parallel to the polarization direction of the incoming laser beam are heated up selectively. Thereby they gain additional energy to re-orientate into an energetically more favorable position.

In conclusion, the combined patterning and alignment capabilities of LDSA offer a considerable potential in both fundamental studies and applied research on organic electronic devices.

References

- [1] L. Pithan, P. Beyer, L. Bogula, A. Zykov, P. Schäfer, J. Rawle, C. Nicklin, A. Opitz, S. Kowarik; **Adv. Mater.** 2016, 1604382. *Direct Photoalignment and Optical Patterning of Molecular Thin Films*
- [2] S. Tavazzi, L. Raimondo, L. Silvestri, P. Spearman, A. Camposeo, M. Polo, D. Pisignano; **J. Chem. Phys.** 2008, 128, 154709
- [3] A. Navarro-Quezada, M. Aiglinger, E. Ghanbari, T. Wagner, P. Zeppenfeld; **Rev. Sci. Instrum.** 2015, 86, 113108.