Hitchhiking triplet states to better understand organic semiconductors

Insights into their structure–function relationship gained by time-resolved EPR spectroscopy

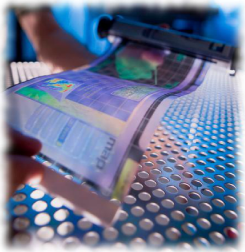
Till Biskup

Seminar der Physikalischen Chemie
Universität Rostock
28.04.2023

Organic Electronics

Closer to Our Daily Lives Than We May Think...

OFETs

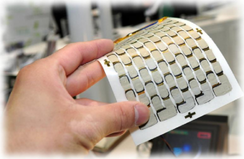


OLEDs

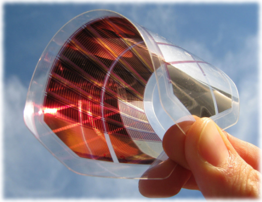
cheap
lightweight

Organic Electronics

printable
flexible



Thermoelectrics



OSCs

Molecules specifically tailored by your favourite synthetic chemist...

Organic Semiconductors

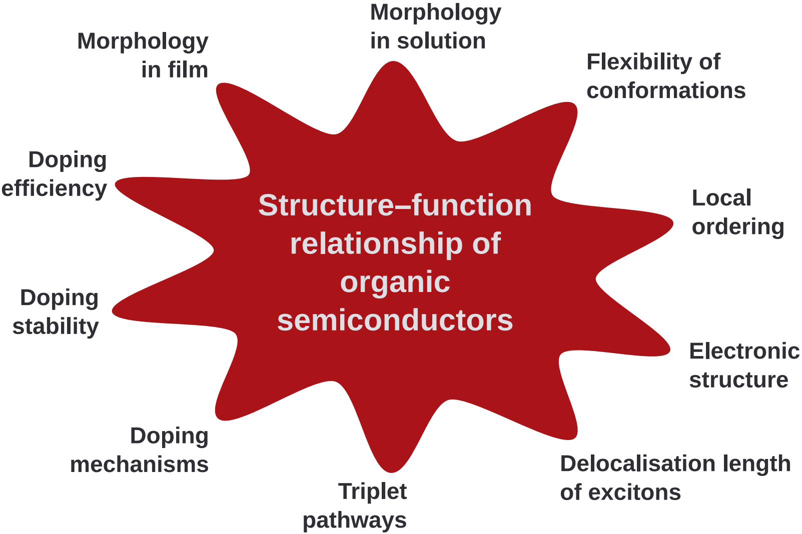
A Series of Advantages Over Their Inorganic Counterparts

Advantages of organic semiconductors

- cheap
- simple processing
- lightweight
- mechanically flexible
- chemically modifiable
- biodegradable

Structure–Function Relationship

Highly Important But Still Barely Understood



Structure–function relationship of organic semiconductors

Morphology in solution

Flexibility of conformations

Local ordering

Electronic structure

Delocalisation length of excitons

Triplet pathways

Doping mechanisms

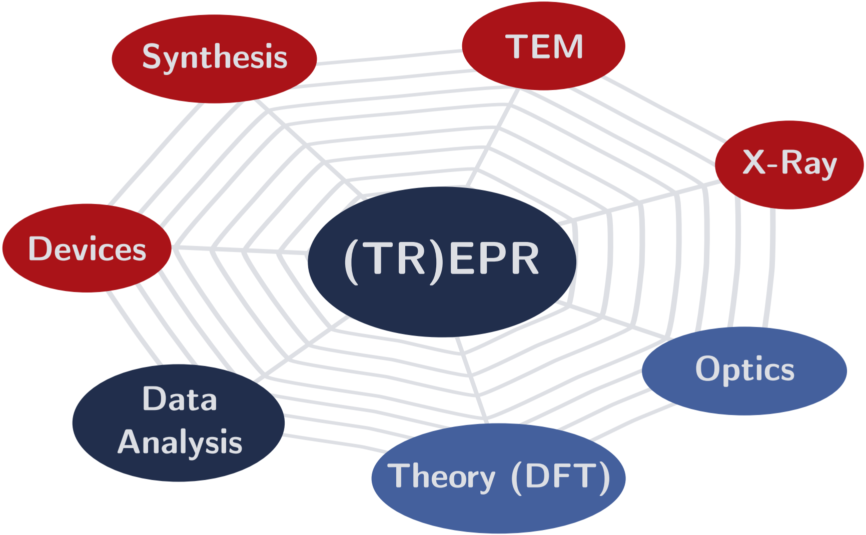
Doping stability

Doping efficiency

Morphology in film

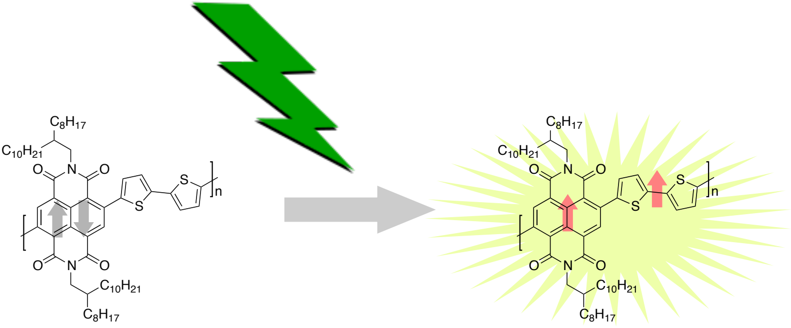
Structure–Function Relationship

A Multidisciplinary Approach to Unravel Some of Its Mysteries



Illuminating Conjugated Polymers…

Creating Paramagnetic Species by Optical Excitation



singlet ground state

diamagnetic

no EPR signal 👎

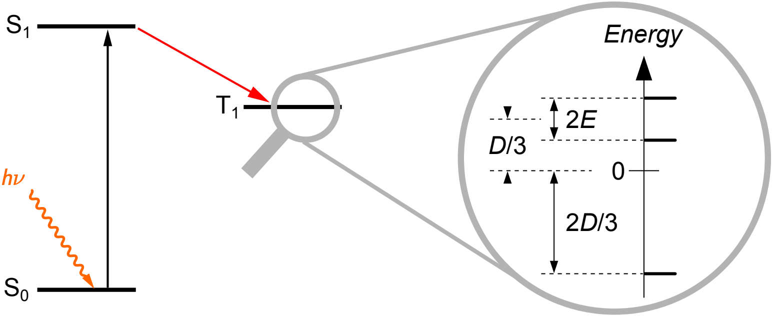
triplet excited state

paramagnetic

EPR signal 👍

The Triplet State: Two Unpaired Electrons

Spin–Spin Interaction: Dipolar Interaction and Zero-Field Splitting

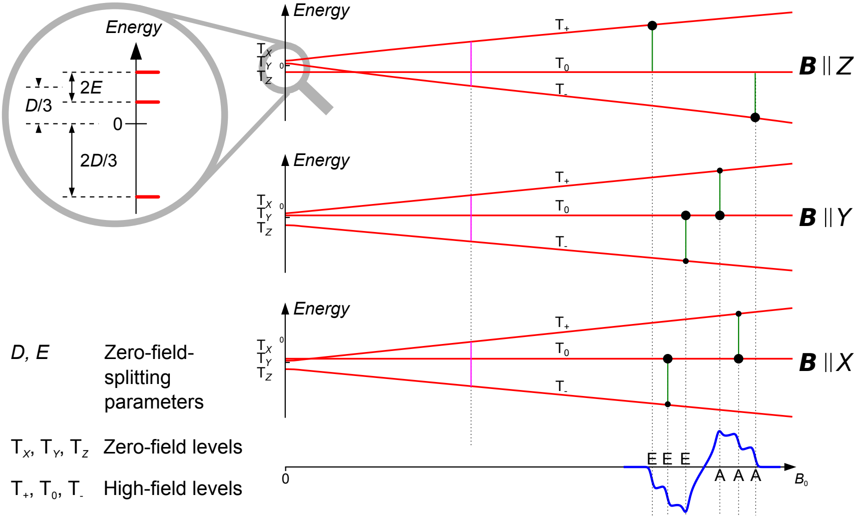


$$\mathcal{H}_{\mathrm{ZFS}} = \boldsymbol{S}\mathbf{D}\boldsymbol{S} \qquad \mathbf{D} = \begin{pmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{pmatrix}$$

modified from: Biskup, *Front. Chem.* **7**:10, 2019

The Triplet State: Two Unpaired Electrons

TREPR Signals of Triplet States Are Intrinsically Orientation-Dependent

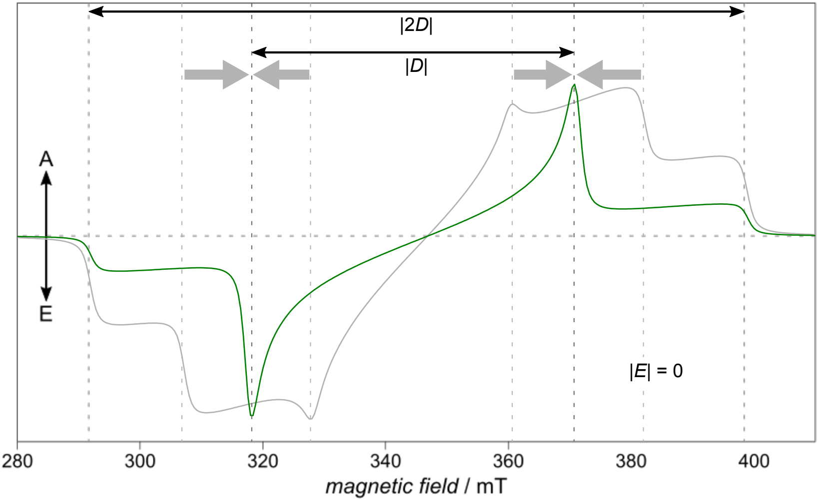


D, *E*	Zero-field-splitting parameters
T_X, T_Y, T_Z	Zero-field levels
T_+, T_0, T_-	High-field levels

modified from: Weber, *eMagRes* **6**:255, 2017

The Triplet State: Two Unpaired Electrons

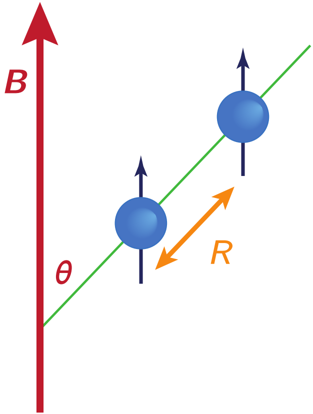
Rhombicity Gets Reflected in Shape of TREPR Spectra



modified from: Biskup, *Front. Chem.* **7**:10, 2019

Systems with Two Unpaired Electron Spins

Some Characteristics Important for EPR Spectroscopy

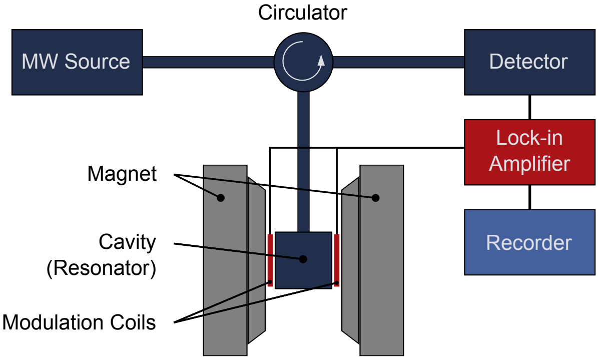


- Interaction depends on distance (R) between spins
- Interaction depends on angle (θ) to magnetic field (B)
- Interaction characterised by two parameters (D and E)
- Light excitation leads to non-Boltzmann population

☛ TREPR can probe both: delocalisation and orientation

Continuous-Wave EPR

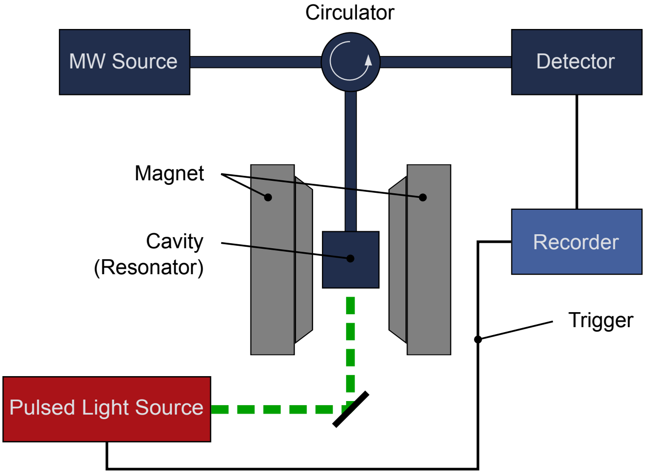
For Stable Species



modified from: Biskup, *Front. Chem.* **7**:10, 2019

Time-Resolved EPR

For Spin-Polarised Species



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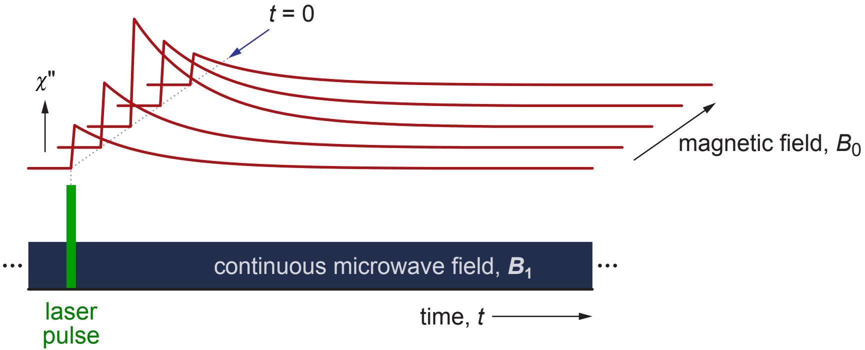
Time-Resolved EPR

Detection Scheme: A Pump-Probe Experiment

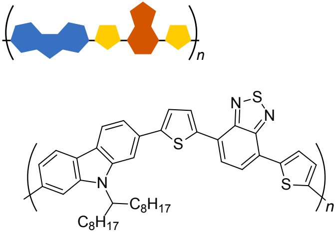


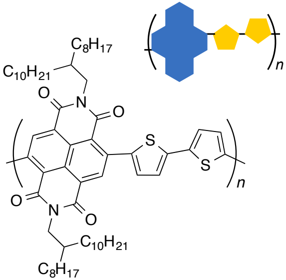
- Stepwise: one field point at a time (whole time trace)
- Direct signal detection (no modulation of magnetic field)
- Time resolution down to 10 ns (typically approx. 100 ns)

modified from: Weber, *eMagRes* **6**:255, 2017

Systems Investigated

Two Prototypical, Yet Different, Polymers





PCDTBT

p-type polymer

amorphous

long-term stable

PNDIT2

n-type polymer

highly crystalline

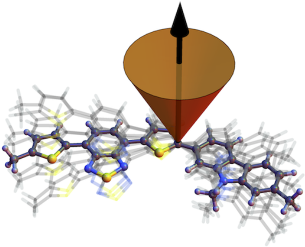
high carrier mobility

Film Morphology

Orientation and Degree of Ordering of a Polymer Film on Substrate

Ordering of PCDTBT Revealed by Time-Resolved Electron Paramagnetic Resonance Spectroscopy of Its Triplet Excitons

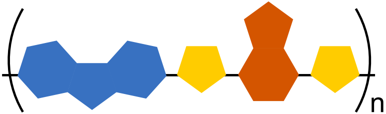
Till Biskup, Michael Sommer, Stephan Rein, Deborah L. Meyer,*
Markus Kohlstädt, Uli Würfel, Stefan Weber



Angew. Chem. Int. Ed. **54**:7707–7710, 2015

Who Is On Stage?

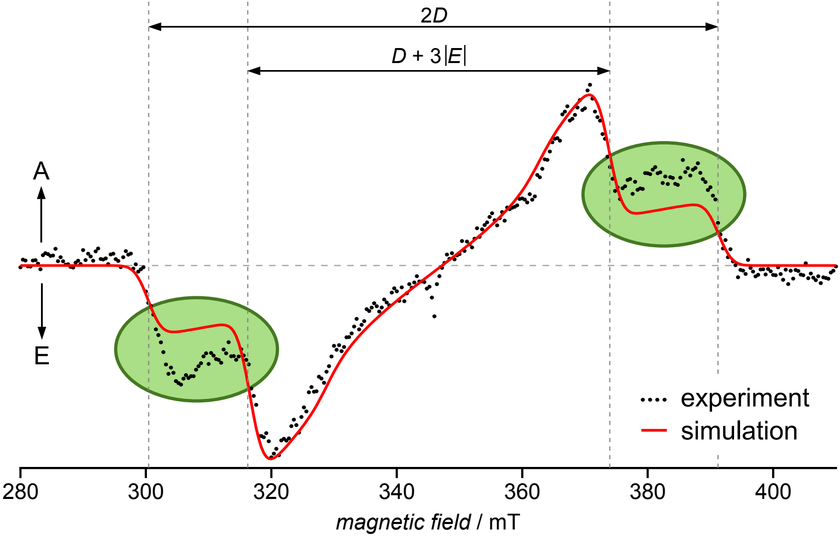
The Polymer PCDTBT



PCDTBT

PCDTBT Shows Partial Ordering

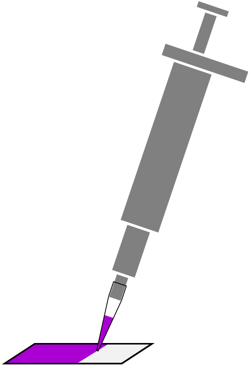
Spectra From Thin Films on Sample Tube Wall Have Shoulders



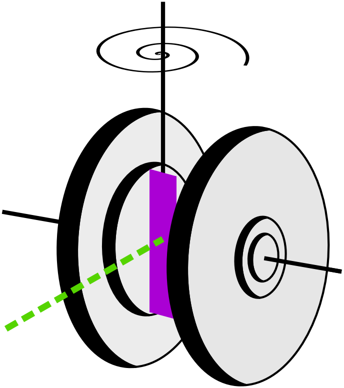
Controlling Sample Morphology

A Defined Sample Morphology for Orientation-Dependent TREPR

1. Drop-cast on substrate

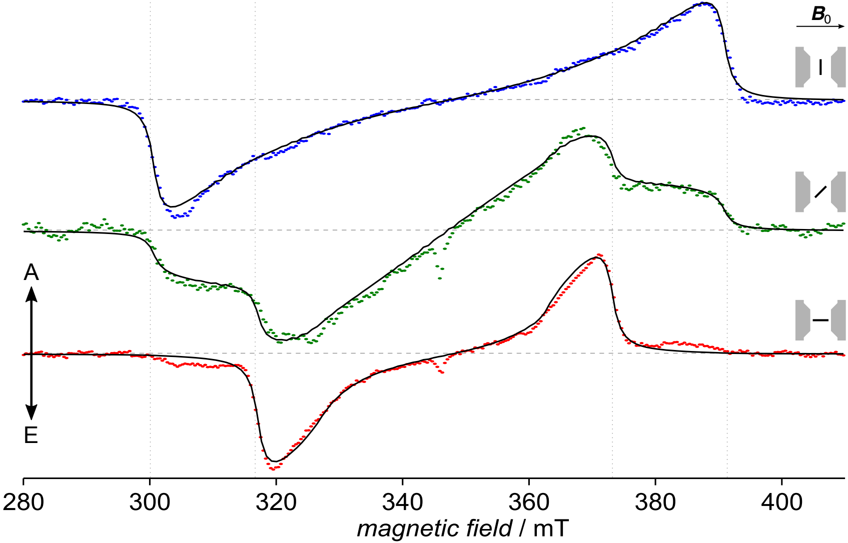


2. Orientation-dependent TREPR



PCDTBT Exhibits Strong Orientational Effects

Using TREPR of the Triplet Excitons to Probe Morphology

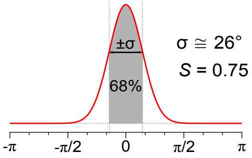


Orientation and Degree of Ordering

Using TREPR of the Triplet Excitons to Probe Morphology

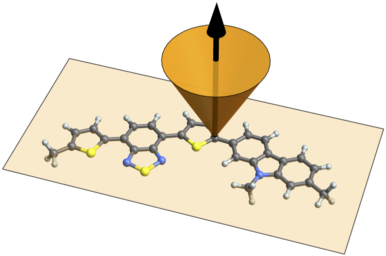
Simulations

- Global fit of all spectra
- Gaussian distribution of orientations



Results

- PCDTBT thin films show strong ordering
- *face-on* orientation



TREPR

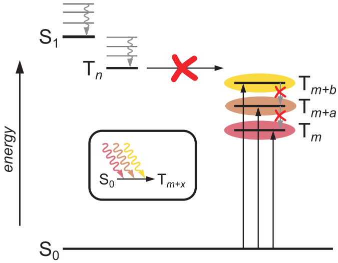
- Reveals both, orientation and degree of ordering
- Probes whole films, not only surfaces

Origins of Triplet States

A Direct Route to Triplets Long Forgotten

Direct $S_0 \rightarrow T$ Excitation of a Conjugated Polymer Repeat Unit: Unusual Spin-Forbidden Transitions Probed by Time-Resolved EPR Spectroscopy

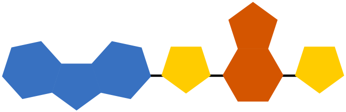
*Deborah L. Meyer, Florian Lombeck, Sven Huettner, Michael Sommer, Till Biskup**



J. Phys. Chem. Lett. **8**:1677–1682, 2017

Who Is On Stage?

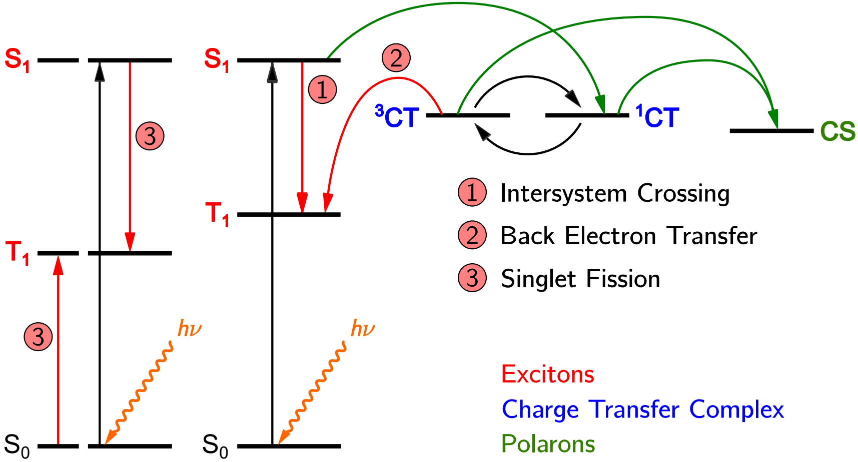
Cbz-TBT, the Repeat Unit of PCDTBT



CbzTBT

Why Bother About Triplets?

Different Routes to Generate Triplet Excitons



① Intersystem Crossing

② Back Electron Transfer

③ Singlet Fission

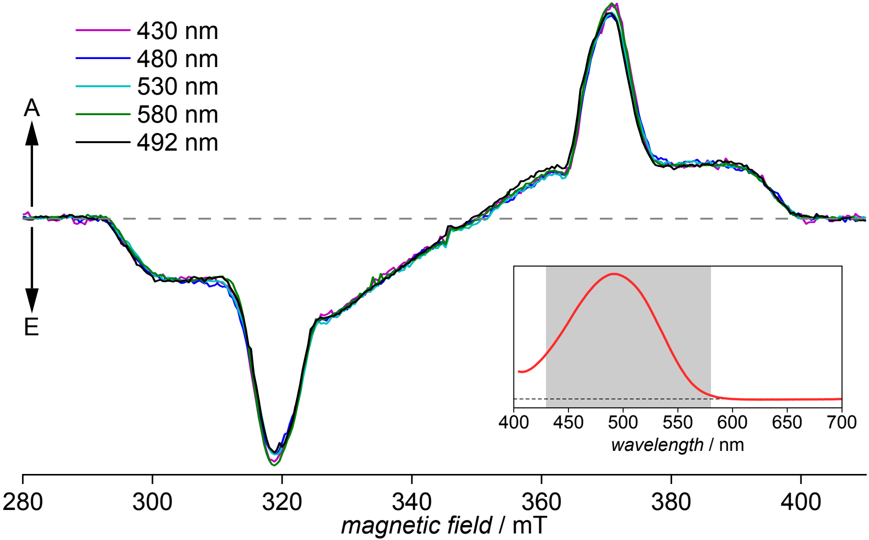
Excitons

Charge Transfer Complex

Polarons

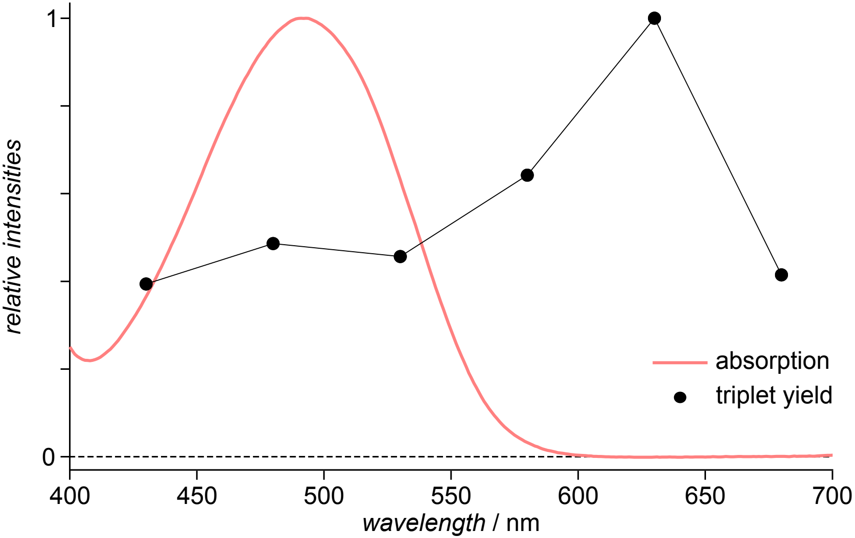
Direct $S_0 \rightarrow T$ Excitation

Exciting CbzTBT Red-Shifted From Its Optical Absorption Band



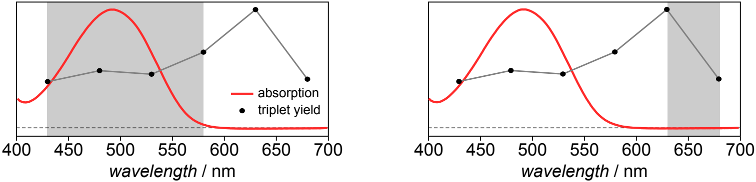
Direct $S_0 \rightarrow T$ Excitation

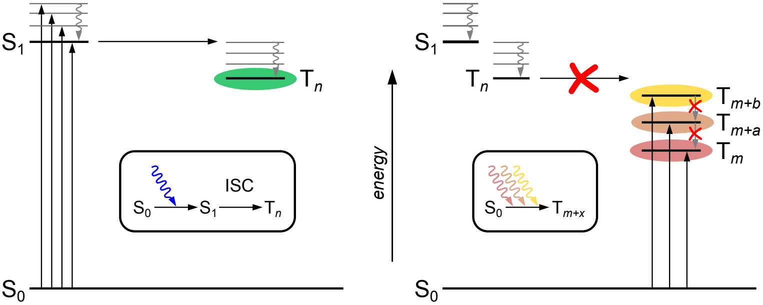
Triplet Yields Are Even Higher Red-Shifted From the Absorption



Direct $S_0 \rightarrow T$ Excitation

Two Different Triplet Routes Within One Molecule





Direct $S_0 \rightarrow T$ excitation: Lewis & Kasha, *J. Am. Chem. Soc.* **67**:994–1003, 1945

Direct $S_0 \rightarrow T$ Excitation

Further Insights From Spectral Simulations of Triplet States

Spectral simulations

- Near-perfect fits for all triplet spectra

Simulation parameters

λ / nm	$\lvert D\rvert$ / MHz	Γ / mT
492	1361.6 ± 3.0	3.42
630	1344.7 ± 1.5	2.08
650	1317.2 ± 1.4	1.83
680	1288.5 ± 1.3	1.54

- ☛ $\lvert D\rvert$ decreases with increasing λ
- ☛ Only Lorentzian linewidths, decreasing with increasing λ

Direct $S_0 \rightarrow T$ Excitation

An Alternative Triplet Route With Potential High Impact

Three results

- Triplet states when excited red-shifted from the CT band
- Triplet yield higher when excited beyond the CT band
- Distinct triplet states

Explanation

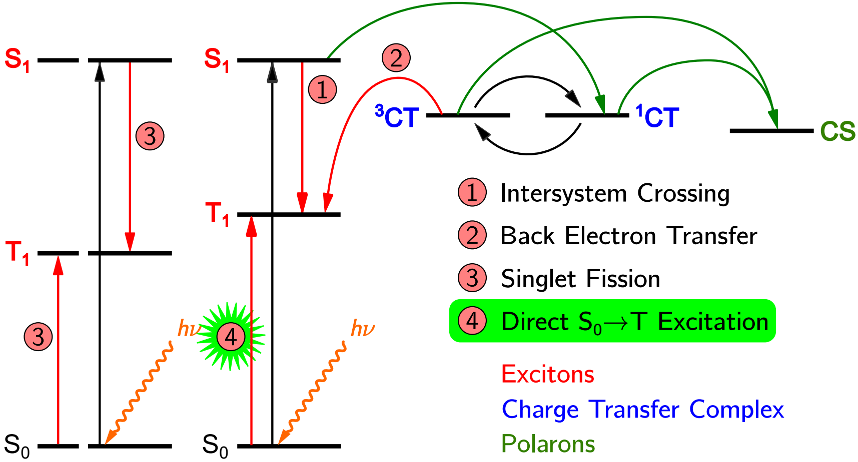
- Direct $S_0 \rightarrow T$ optical transition
- Lower yield of $S_1 \rightarrow T$ transition due to competing processes

TREPR

- Reveals origin of triplet states
- Unequivocally assigns triplet states

Different Routes Towards Triplet Excitons

A More Complete Picture Including Direct $S_0 \rightarrow T$ Excitation



1. Intersystem Crossing
2. Back Electron Transfer
3. Singlet Fission
4. Direct $S_0 \rightarrow T$ Excitation

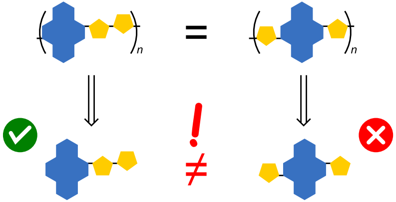
Excitons
Charge Transfer Complex
Polarons

Electronic Structure

Identifying the Building Block of a Polymer

Know your building blocks: Time-resolved EPR spectroscopy reveals NDI-T2 and not T-NDI-T to resemble the electronic structure of PNDIT2

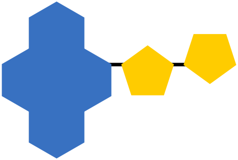
*Clemens Matt, Rukiya Matsidik, Deborah L. Meyer, Mirjam Schröder, Michael Sommer, Till Biskup**



Org. Electron. **117**:106790, 2023

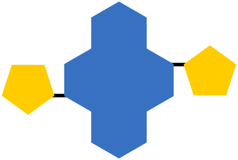
Who Is On Stage?

NDI-T2 and T-NDI-T, Two Potential Repeat Units of PNDIT2



NDI-T2

A-D-D

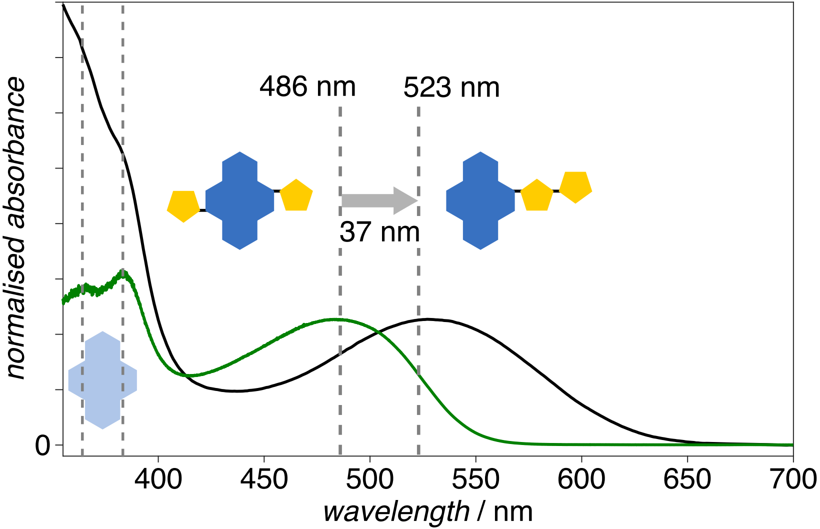


T-NDI-T

D-A-D

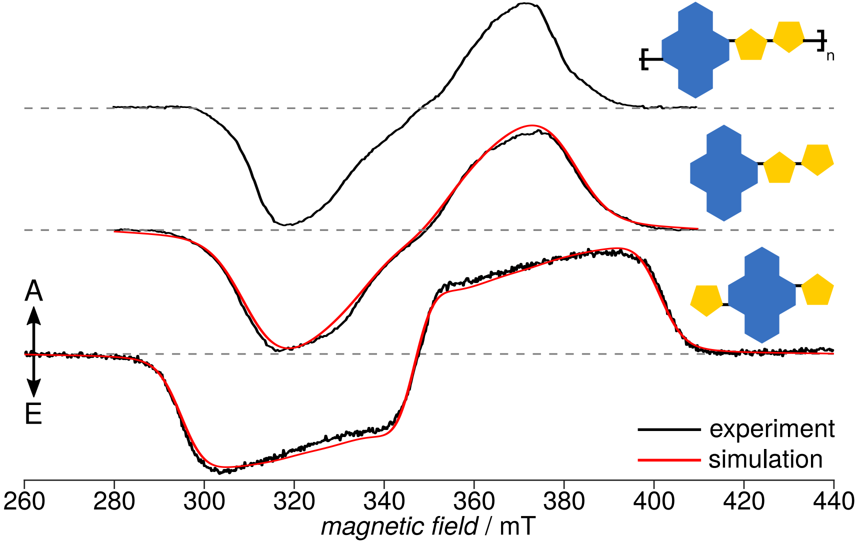
Electronic Structure

Steady-State Optical Spectroscopy is Inconclusive



Electronic Structure

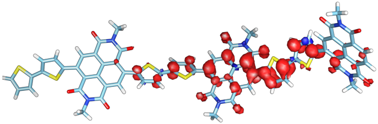
TREPR Spectroscopy to the Rescue



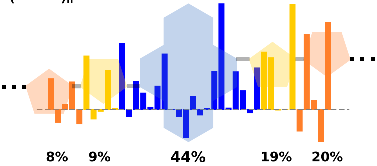
Quantum-Chemical Calculations (I)

Spin Density Calculations Provide Further Insight

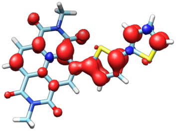
PNDIT2



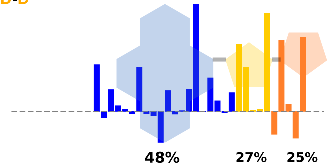
(A-D-D)$_n$



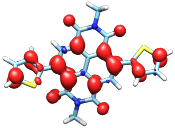
NDI-T2



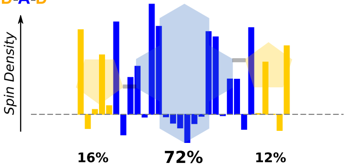
A-D-D



T-NDI-T



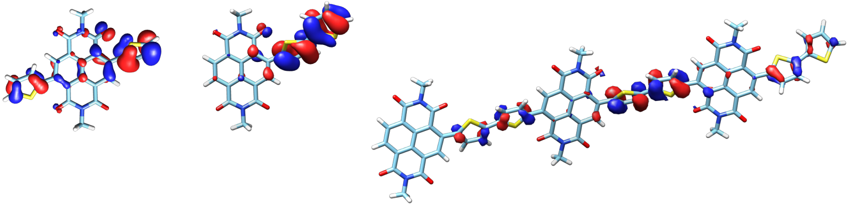
D-A-D



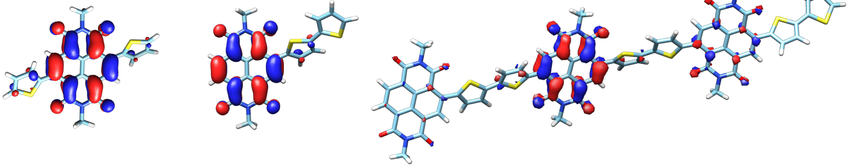
Quantum-Chemical Calculations (II)

NTO Reveal Triplet and Singlet States to be Consistent

Hole



Particle



T-NDI-T **NDI-T2** **PNDIT2**

Identifying the Building Block of a Polymer

Highly Relevant Detailed Insights From TREPR Spectroscopy

Triplet simulation parameters

	$\lvert D\rvert$ / MHz	$\lvert E\rvert/\lvert D\rvert$	Γ_G / mT	Γ_L / mT	$p_{1,2,3}$
PNDIT2	1095 ± 4.3	0.206	7.0 ± 0.8	2.1 ± 0.4	0.00, 0.24, 0.76
NDI-T2	1143 ± 2.0	0.270	10.9 ± 0.6	6.5 ± 0.5	0.00, 0.00, 1.00
T-NDI-T	1500 ± 0.8	0.333	8.0 ± 0.3	3.0 ± 0.2	0.00, 1.00, 0.00

Results

- NDI-T2 resembles the electronic structure of PNDIT2
- QC calculations are consistent with TREPR spectroscopy

TREPR

- Highly relevant detailed insights into the electronic structure
- Superior molecular resolution compared to optical spectroscopy

Structure–Function Relationship

Summary: Aspects That Can Be Addressed Using (TR)EPR Spectroscopy

Structure–function relationship of organic semiconductors

Morphology in solution

Flexibility of conformations

Local ordering

Electronic structure

Delocalisation length of excitons

Triplet pathways

Doping mechanisms

Doping stability

Doping efficiency

Morphology in film

Review: Biskup, *Front. Chem.* **7**:10, 2019

Structure–Function Relationship

Summary: Aspects That Can Be Addressed Using (TR)EPR Spectroscopy

Film Morphology

- Information on both, orientation and degree of ordering
- Triplet spectra highly sensitive to partial orientation

Triplet Routes

- Direct access to triplet states, unequivocally identifiable
- Triplet populations can reveal underlying ISC mechanism

Electronic Structure

- Information beyond exciton delocalisation
- Triplet populations highly sensitive to local environment

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(Mostly) Freiburg

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Gesellschaft
Freiburg

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Thank you for your attention!