

Hyperpolarised Electron Spins as a Sensitive Probe for Investigating Structure–Function Relationship in Organic Energy Materials

Till Biskup

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DS 7 Spins in Molecular Systems:

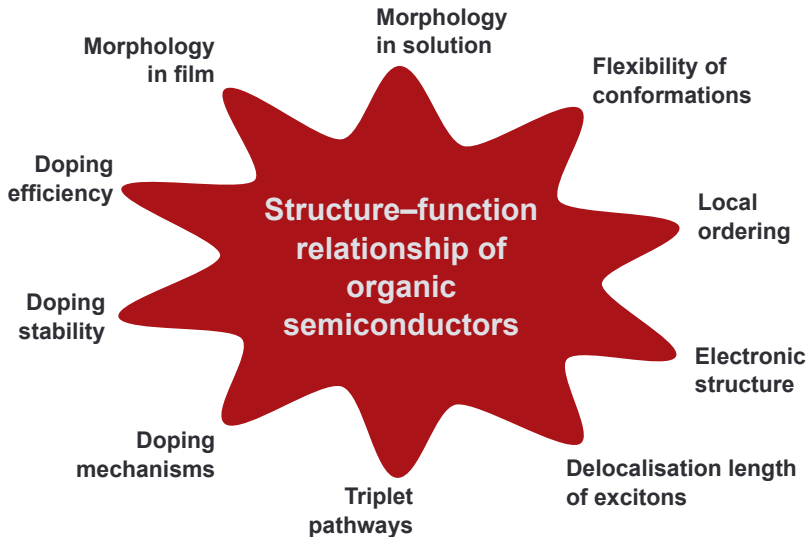
Strategies and Effects of Hyperpolarisation

19.03.2025



Structure–Function Relationship

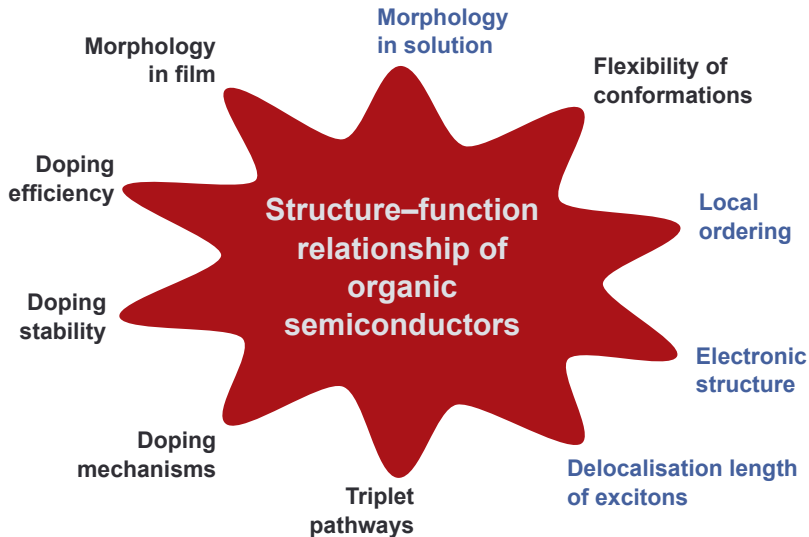
Aspects That Can Be Addressed Using (TR)EPR Spectroscopy



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

Structure–Function Relationship

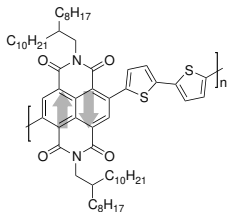
Aspects That Can Be Addressed Using (TR)EPR Spectroscopy



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Illuminating Conjugated Polymers...

Creating Hyperpolarised Paramagnetic Species by Optical Excitation



singlet ground state

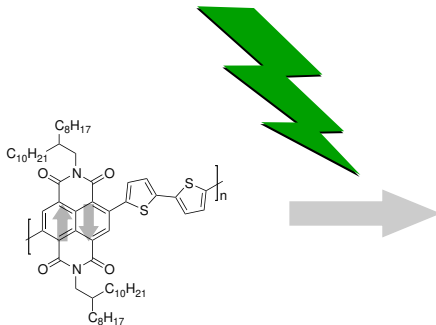
diamagnetic

no EPR signal



Illuminating Conjugated Polymers...

Creating Hyperpolarised Paramagnetic Species by Optical Excitation



singlet ground state

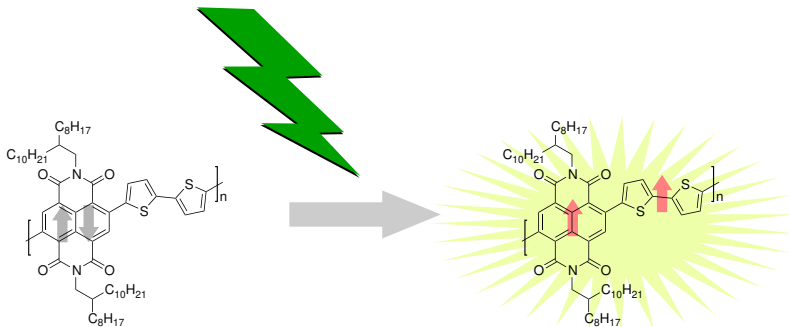
diamagnetic

no EPR signal



Illuminating Conjugated Polymers...

Creating Hyperpolarised Paramagnetic Species by Optical Excitation



singlet ground state

diamagnetic

no EPR signal



triplet excited state

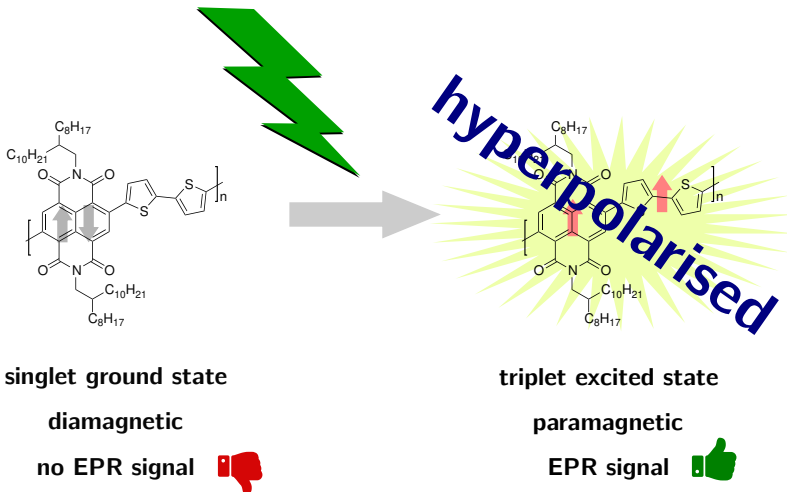
paramagnetic

EPR signal



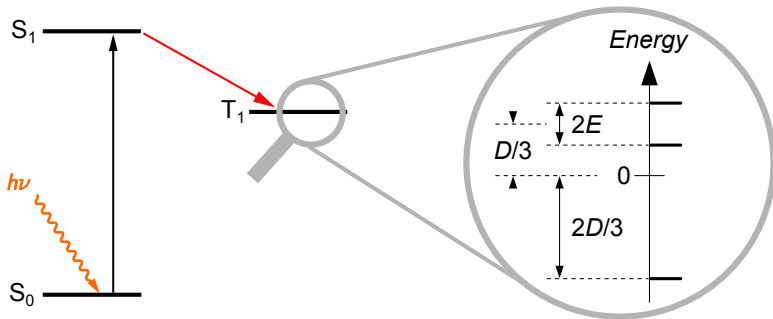
Illuminating Conjugated Polymers...

Creating Hyperpolarised Paramagnetic Species by Optical Excitation



The Triplet State: Two Unpaired Electrons

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



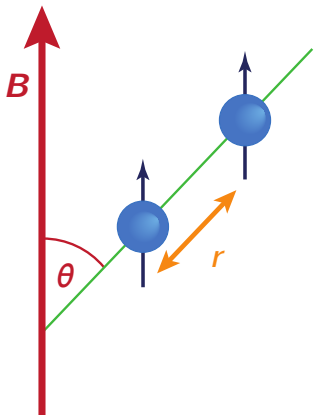
$$\mathcal{H}_{\text{ZFS}} = \mathbf{S} \mathbf{D} \mathbf{S}$$

$$\mathbf{D} = \begin{pmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{pmatrix}$$

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

The Triplet State: Two Unpaired Electrons

Some Characteristics Important for EPR Spectroscopy

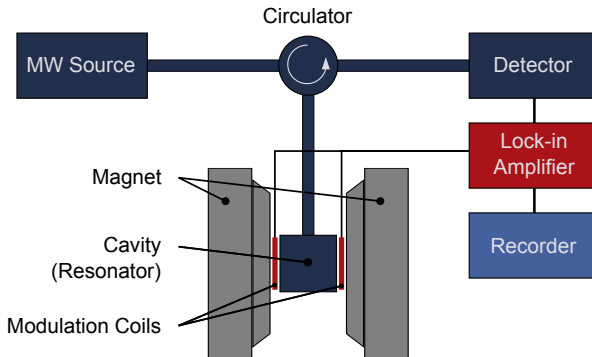


- ▶ Interaction *inversely* depends on distance (r) between spins
- ▶ Interaction depends on angle (θ) to magnetic field (B)
- ▶ Interaction characterised by two parameters (D and E)
- ▶ Light excitation leads to non-Boltzmann population (hyperpolarisation)

☛ TREPR can probe both: delocalisation and orientation

Continuous-Wave EPR

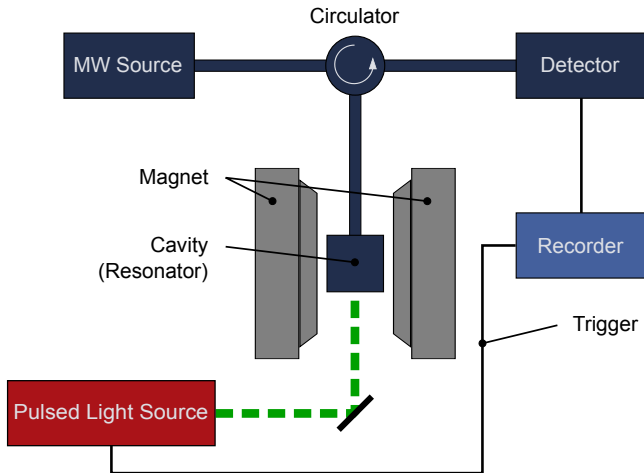
For Stable Species



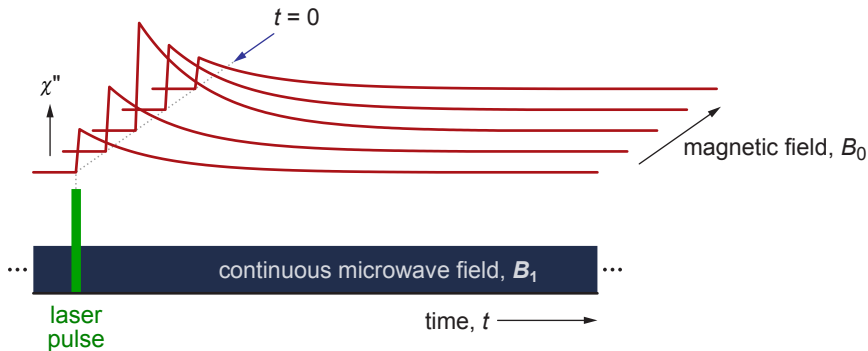
modified from: Biskup, *Front. Chem.* 7:10, 2019

Time-Resolved EPR

For Spin-Polarised Species, *i.e.* Non-Boltzmann Spin States



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

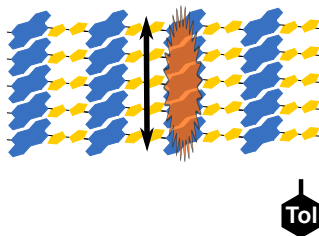
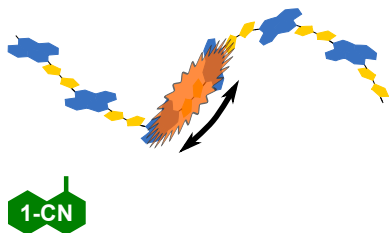


- ▶ Stepwise: one field point at a time (whole time trace)
- ▶ Direct signal detection (no modulation of magnetic field)
- ▶ Time resolution down to 10 ns (typically approx. 100 ns)
- ▶ Typically only slices along B_0 at fixed time are shown/analysed

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

Solvent-Mediated Aggregate Formation of PNDIT2: Decreasing the Available Conformational Subspace by Introducing Locally Highly Ordered Domains

*Deborah L. Meyer, Rukiya Matsidik, Sven Huettner, Michael Sommer, Till Biskup**



Phys. Chem. Chem. Phys. **20**:2716–2723, 2018

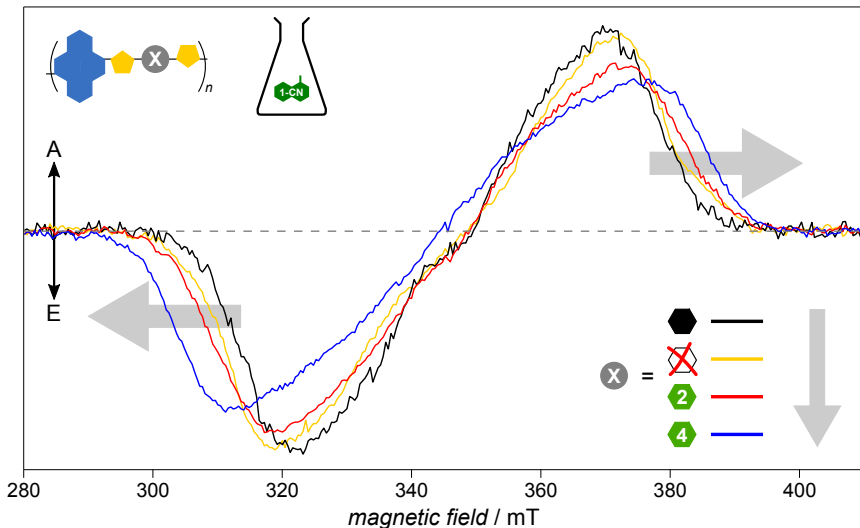
Systematically Varying the Backbone of PNDIT2: Impact on Exciton Delocalisation and Local Ordering in Aggregates

*Katja Stry, Paul Jung, Rukiya Matsidik, Michael Sommer, Till Biskup**



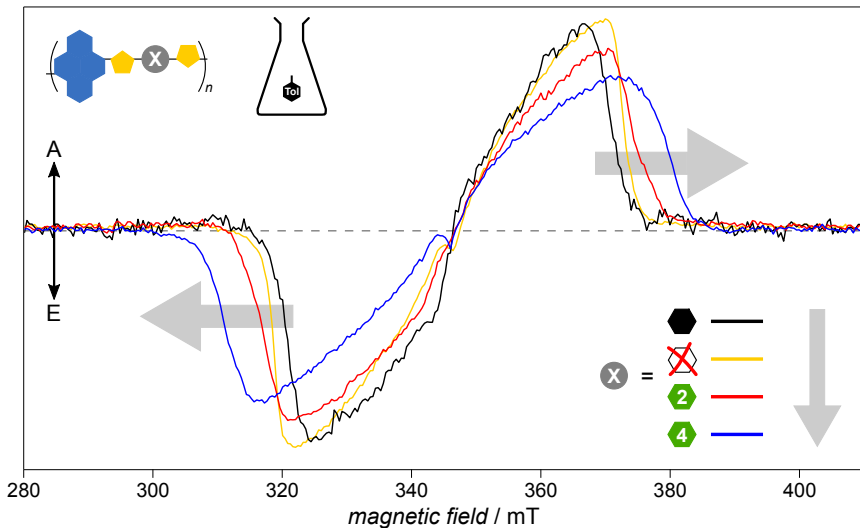
Systematically Extending the Backbone

TREPR Spectra in the "Good" Solvent 1-CN



Systematically Extending the Backbone

TREPR Spectra in the "Bad" Solvent Tol



Systematically Extending the Backbone

Insight from Simulation Parameters of the TREPR Spectra













		λ_{ex}	$ D $	$ E $	$ E / D $	Γ_G	Γ_L
		622	1095	226	0.21	7.00	2.10
		603	909	282	0.31	6.50	5.69
		574	1097	256	0.23	9.80	2.46
		544	1231	303	0.25	8.63	1.59
		702	755	251	0.33	1.40	1.80
		655	701	228	0.33	2.49	2.32
		639	804	266	0.33	5.56	1.37
		590	953	313	0.33	1.62	2.77

$[\lambda_{\text{ex}}] = \text{nm}; [D, E] = \text{MHz}; [\Gamma_G, \Gamma_L] = \text{mT}$

Systematically Extending the Backbone

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Impact of the solvent

- ▶ 1-CN: polymer chain fully solvated, Tol: ordered aggregates
- ▶ Identical situation as known from PNDIT2

Impact of extending the backbone (I): solvated backbone

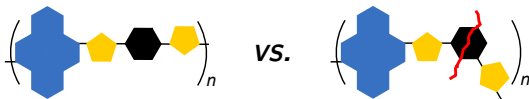
- ▶ Extending the backbone with phenyl extends exciton delocalisation
- ▶ Fluorinating the phenyl reduces exciton delocalisation

Impact of extending the backbone (II): ordered aggregates

- ▶ Extending the backbone with phenyl extends aggregate size
- ▶ Fluorinating the phenyl reduces aggregate size

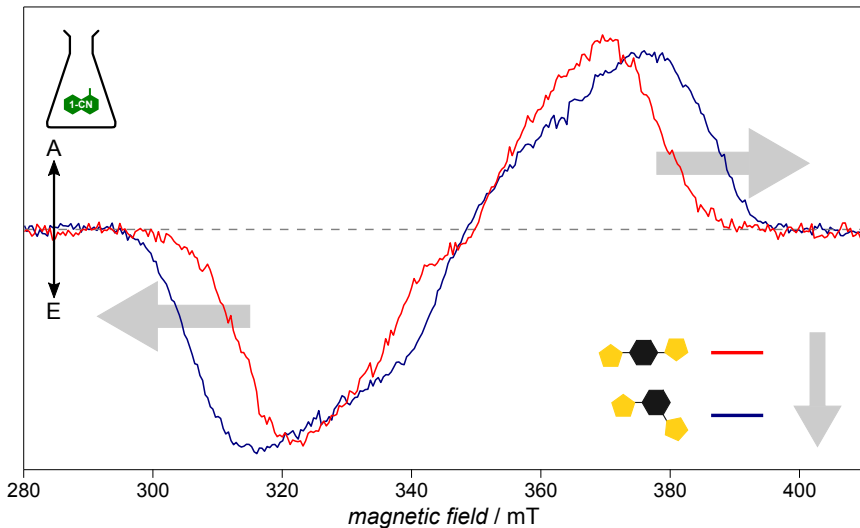
meta-Substituted Backbone Results in Conjugation Break and Disturbs Ordering in Aggregates Due to Increased Disorder

*Paul Jung, Rukiya Matsidik, Younghun Shin, Michael Sommer, Till Biskup**



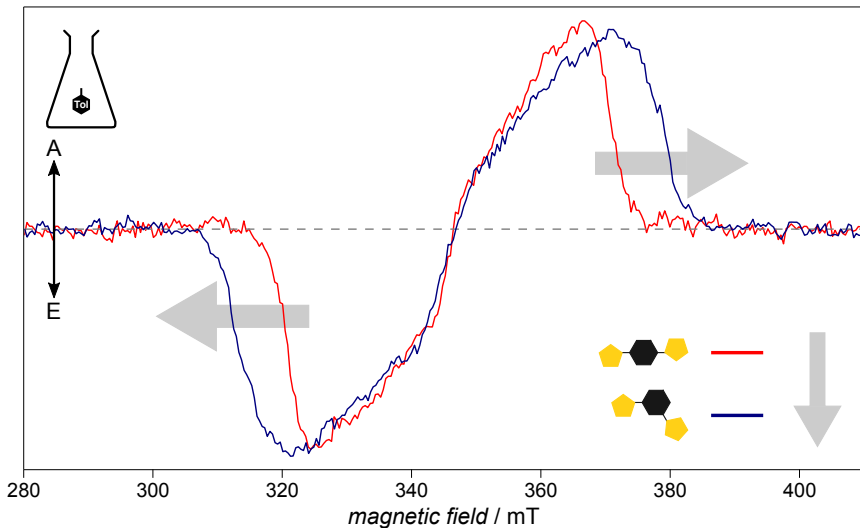
Conjugation Break Upon *meta*-Substitution

TREPR Spectra in the "Good" Solvent 1-CN



Conjugation Break Upon *meta*-Substitution







TREPR Spectra in the "Bad" Solvent Tol



Conjugation Break Upon *meta*-Substitution

Insight from Simulation Parameters of the TREPR Spectra



		λ_{ex}	$ D $	$ E $	$ E / D $	Γ_{G}	Γ_{L}
		603	909	282	0.31	6.5	5.7
		553	1130	346	0.31	11.7	0.8
		655	701	228	0.33	2.5	2.3
		588	922	269	0.29	6.4	1.9

$$[\lambda_{\text{ex}}] = \text{nm}; [D, E] = \text{MHz}; [\Gamma_{\text{G}}, \Gamma_{\text{L}}] = \text{mT}$$

Conjugation Break Upon *meta*-Substitution

Insight from Simulation Parameters of the TREPR Spectra



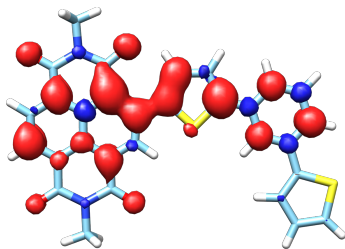
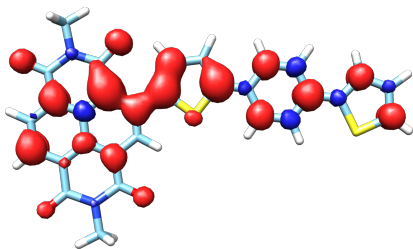
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$[\lambda_{\text{ex}}] = \text{nm}$; $[D, E] = \text{MHz}$; $[\Gamma_G, \Gamma_L] = \text{mT}$

- Conjugation break clearly reflected in higher exciton localisation (larger $|D|$ parameter, $|D| \propto r^{-3}$).
- Smaller and less ordered aggregates in *meta*-substituted backbone (larger $|D|$ parameter, larger inhomogeneity Γ_G).

Conjugation Break Upon *meta*-Substitution

Insight from Spin Density Distribution Calculations



- Conjugation break clearly reflected in higher localisation of spin density distribution.
- Spectroscopy and quantum-chemical calculations nicely agree regarding exciton delocalisation

Theory level: B3LYP/6-31G**

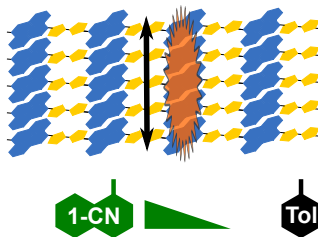
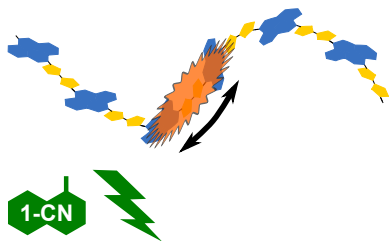
Cooling Rate Determines Aggregation

A Simple Tool to Control Aggregate Formation



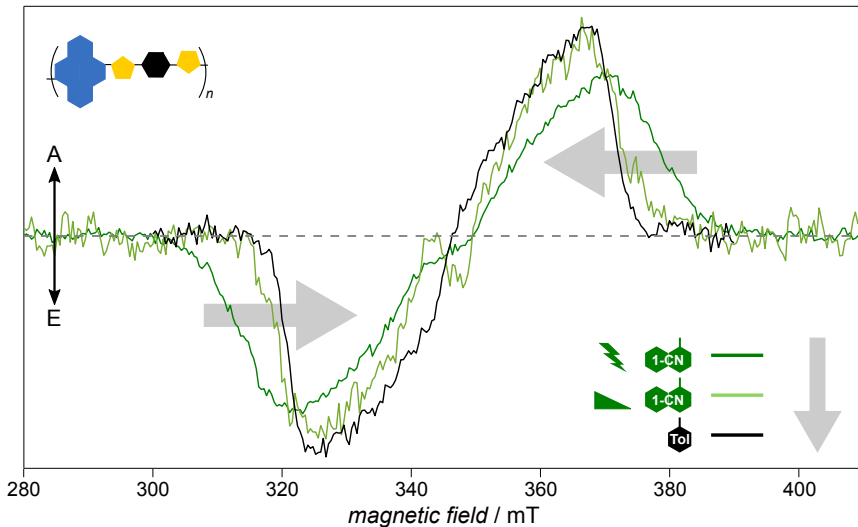
Cooling Rate Determines Aggregate Formation and Exciton Delocalisation Mode Regardless of the Solvent

*Paul Jung, Rukiya Matsidik, Younghun Shin, Michael Sommer, Till Biskup**



Cooling Rate Determines Aggregation







TREPR Spectra of the *para*-Substituted Backbone



Cooling Rate Determines Aggregation

Summary of the Results



			λ_{ex}	$ D $	$ E $	$ E / D $	Γ_G	Γ_L
			603	909	282	0.31	6.5	5.7
			655	749	241	0.32	0.3	5.6
			655	701	228	0.33	2.5	2.3

$$[\lambda_{\text{ex}}] = \text{nm}; [D, E] = \text{MHz}; [\Gamma_G, \Gamma_L] = \text{mT}$$

Cooling Rate Determines Aggregation

Summary of the Results



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$$[\lambda_{\text{ex}}] = \text{nm}; [D, E] = \text{MHz}; [\Gamma_G, \Gamma_L] = \text{mT}$$

- ☛ Slow cooling results in ordered aggregate formation – even in the “good” solvent!
- ☛ Slow cooling in 1-CN results in high homogeneity (small Γ_G), but still smaller aggregates than in Tol ($|D_{\text{Tol}}| < |D_{1\text{-CN}}|$)

① Systematically extending the backbone

- ▶ Incorporating phenyl increases, fluorination of phenyl decreases delocalisation and size/ordering of aggregates

② Conjugation break upon *meta*-substitution

- ▶ Conjugation break decreases delocalisation and size of aggregates

③ Cooling rate determines aggregation

- ▶ Slow cooling induces ordered aggregate formation in any solvent

① Systematically extending the backbone

- ▶ Incorporating phenyl increases, fluorination of phenyl decreases delocalisation and size/ordering of aggregates

② Conjugation break upon *meta*-substitution

- ▶ Conjugation break decreases delocalisation and size of aggregates

③ Cooling rate determines aggregation

- ▶ Slow cooling induces ordered aggregate formation in any solvent

The case for TREPR spectroscopy

- ☞ Probes both, extent and mode of exciton delocalisation
- ☞ Access, *i.a.*, to local homogeneity via line-width analysis
- ☞ Probes optically intransparent samples (high concentration, frozen)

Acknowledgements



People

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Thank you for your attention!