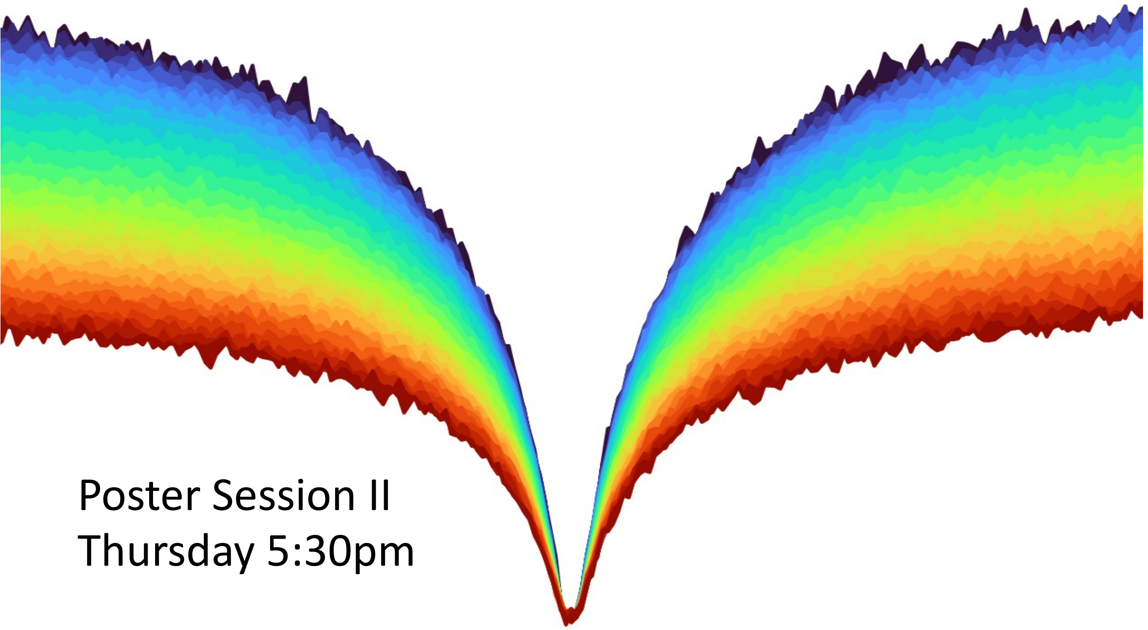
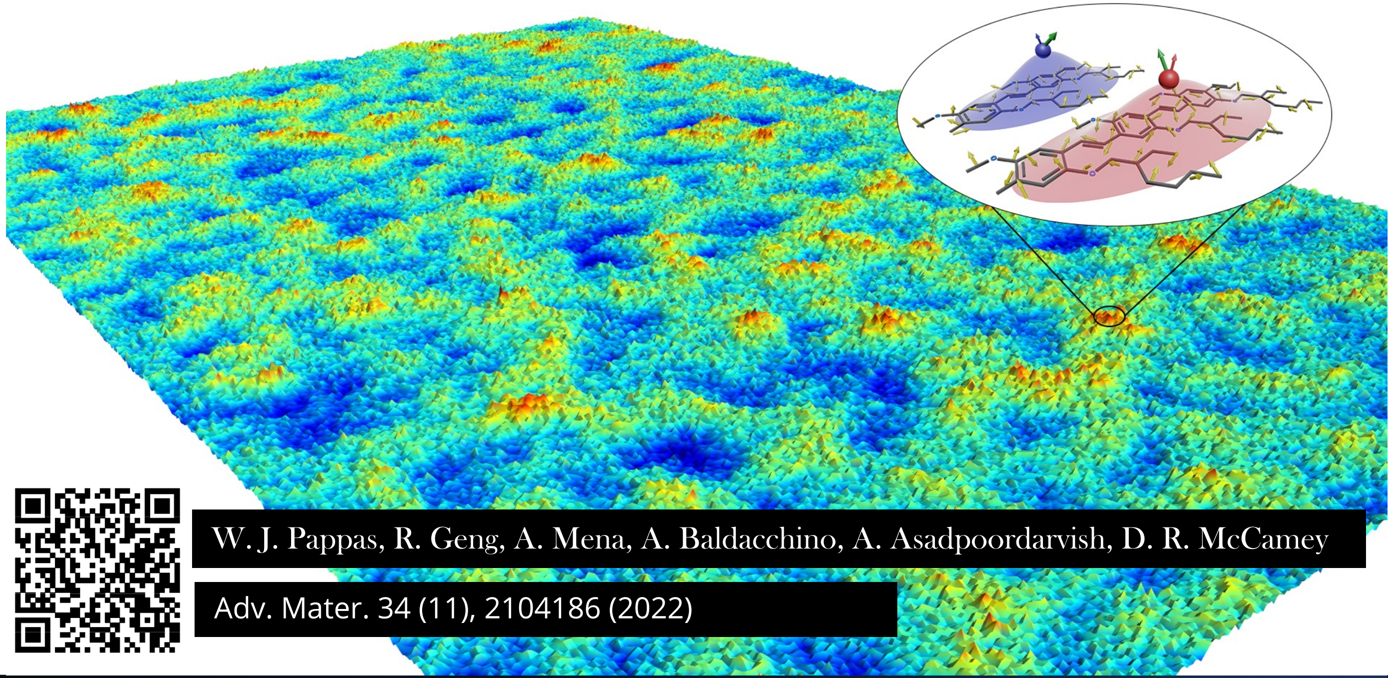


Poster Session II
Thursday 5:30pm



W. J. Pappas, R. Geng, A. Mena, A. Baldacchino, A. Asadpoordarvish, D. R. McCamey

Adv. Mater. 34 (11), 2104186 (2022)

Imaging the Spatial, Temporal and Energetic Landscape of Spin Processes in Organic Optoelectronic Devices

Resolving Spin in Organic Light-Emitting Diodes

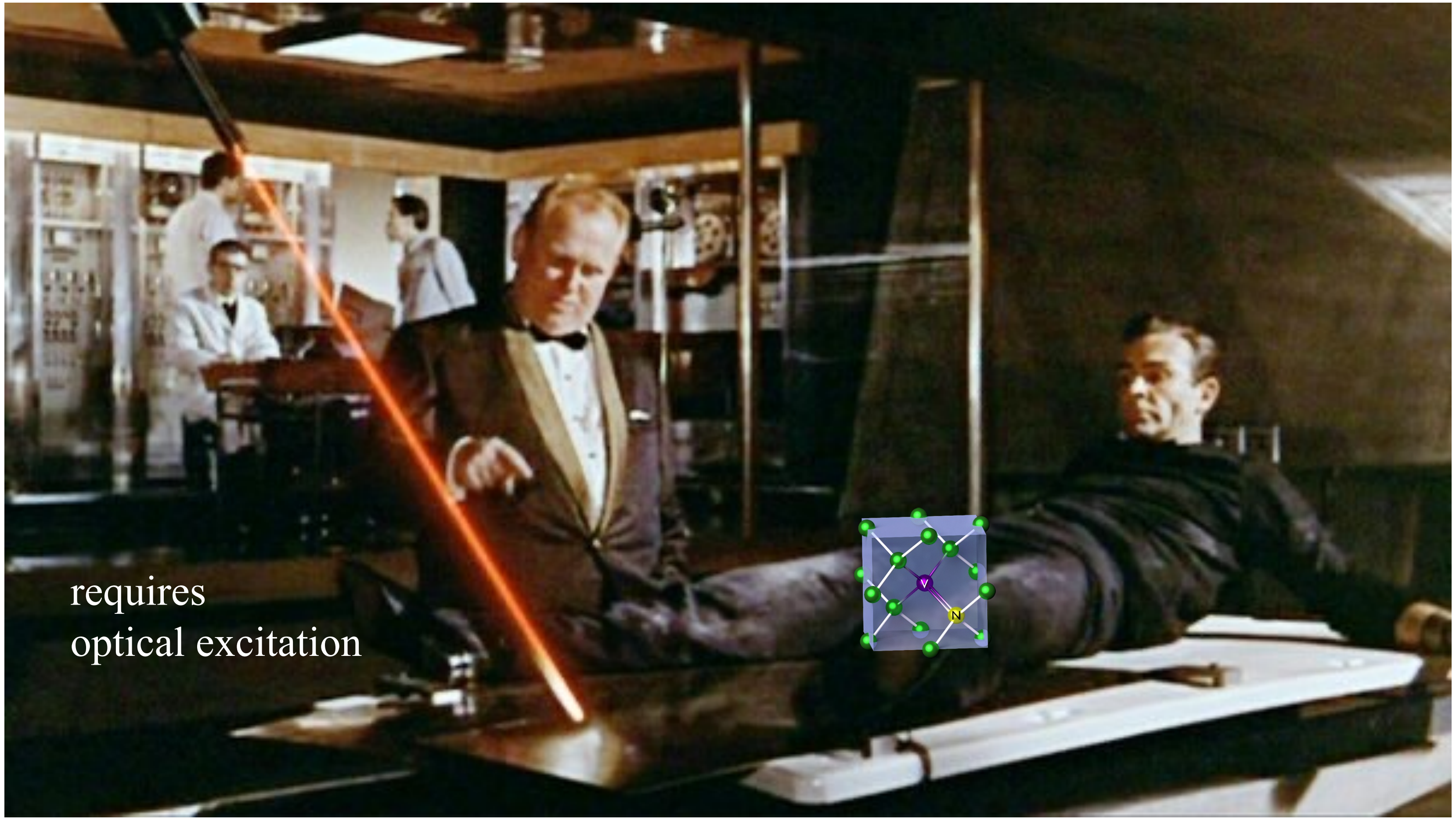
William Pappas

McCamey Lab, UNSW Sydney

Australian Research Council Centre of Excellence in exciton science

NV Centres are amazing sensors!

high sensitivity, high resolution, versatile, and more…

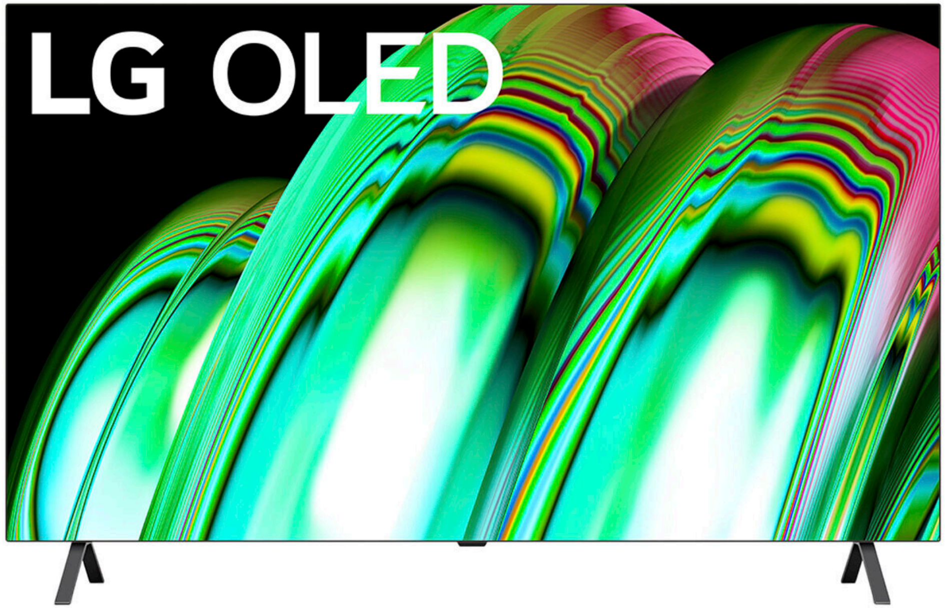


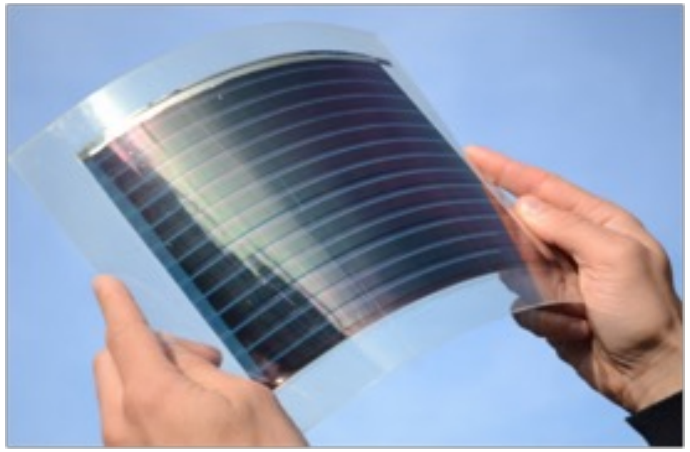
laser limits compactness and integrability, drift, can be expensive, scalability?

Organic Electronics

Commercially available technologies integrating organic electronic materials

© Samsung





© Eight19

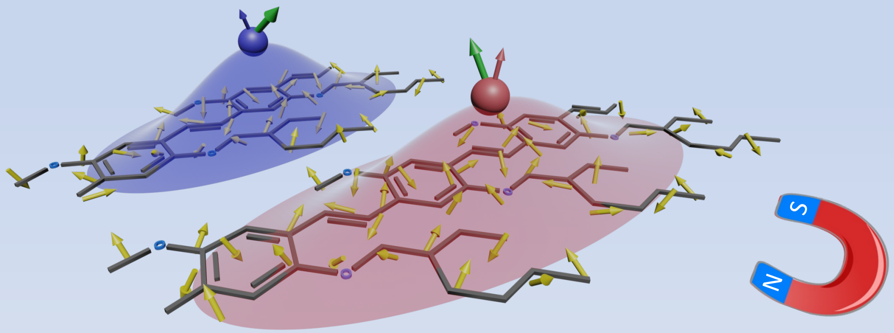
- Electrical operation, laser free
- Cheap, flexible, printable
- Readily modified by synthetic chemistry
- Proven scalability, existing industrial infrastructure

Can spin be used to influence useful properties of these materials?

Australian Research Council
Centre of Excellence in
exciton science

Exploiting the **Quantum Properties** of Materials in Organic Semiconductors

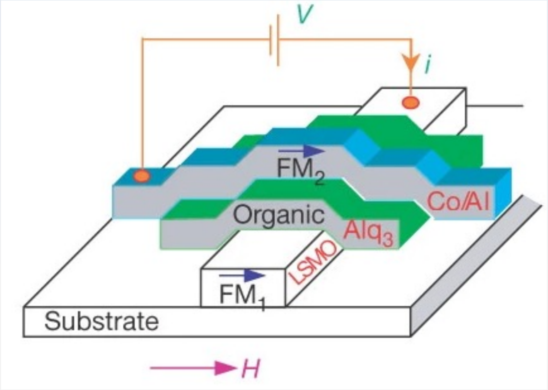
organic materials exhibit weak spin-orbit coupling – long τ_s and l_s
spin properties can be tuned using the tools of synthetic chemistry
understanding **microscopic variation** critical for device performance

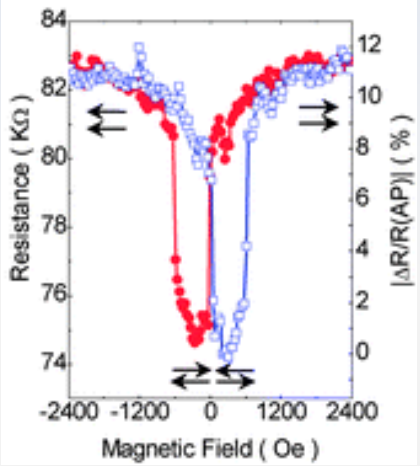


Organic Spintronics

Spin Polarisation Effects

Injection, manipulation and transport of spin polarised current



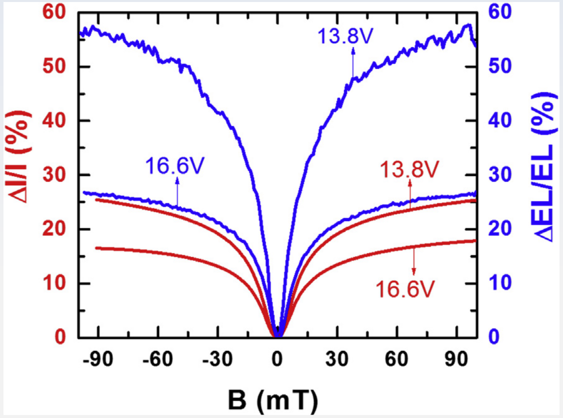


Z. H. Xiong, Di Wu, Z. Valy Vardeny & Jing Shi, *Nature* **427**, 821–824 (2004)

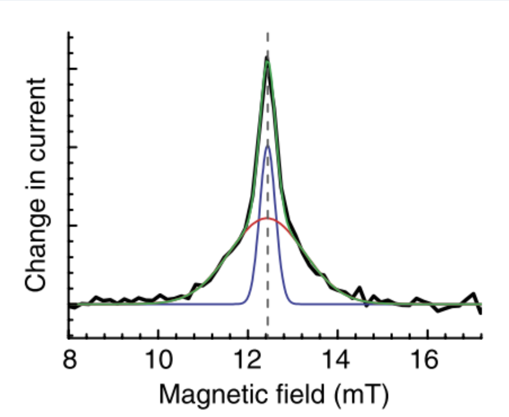
Intrinsic Spin Effects

Spin-Mixing Effects

Modulating singlet and triplet excited state populations



T. D. Nguyen *et al.*, *Phys. Rev. B* **77**, 235209 (2008)



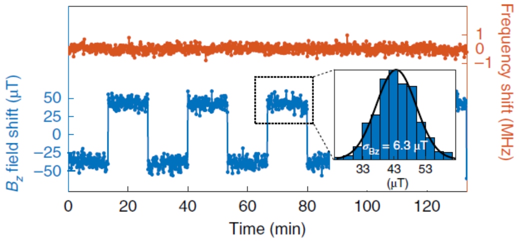
W. Baker *et al.*, *Nat Commun* **3**, 898 (2012)

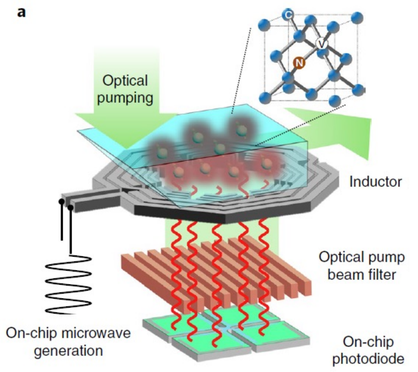
Hybrid Quantum Systems - macroscopic quantum behaviour of molecular systems

Quantum sensing: NV Diamond

- Integrating molecular spins into quantum circuits

*D. Kim et al., Nature Electronics, **2** (7), 284–289 (2019)*

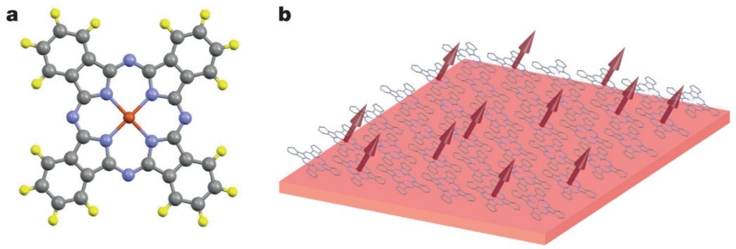




Collective Spin Modes: Simple Molecular Magnets

- Couple many molecular spins to a single resonant mode

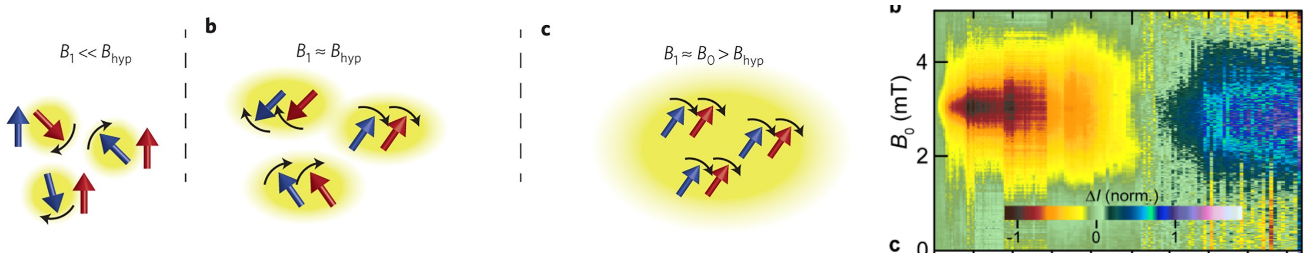
*A. W. Eddins et al., Phys. Rev. Lett. **112**, 120501 (2014)*



Cooperative Spin Phenomena: Spin-Dicke Effect

- Cooperative Larmor precession of spins under ESR in polymer thin-film OLED

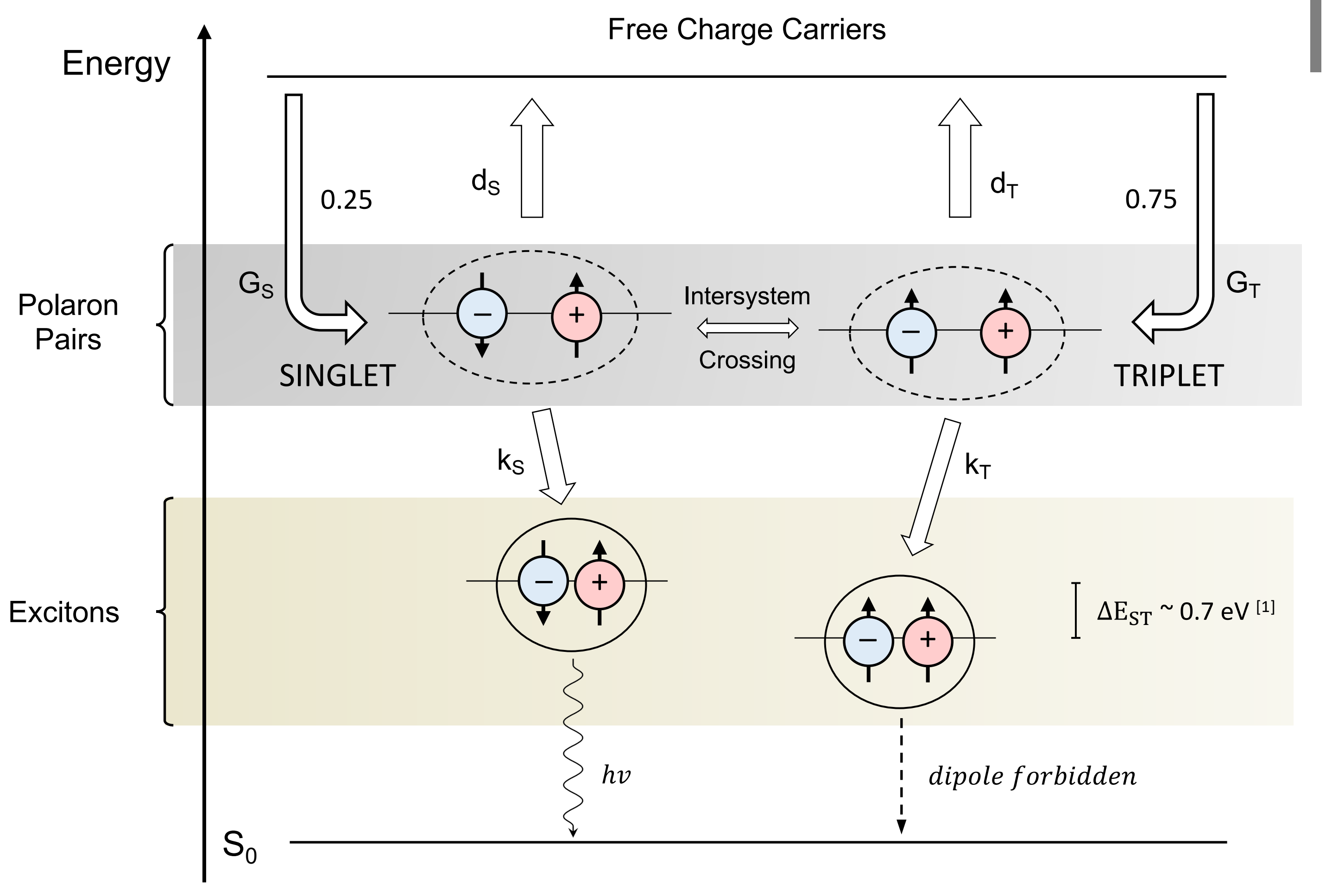
*D. P. Waters et al., Nature Physics, **11**, 910–914 (2015)*



Spin ensembles: deal with **variation** in local spin environment
- distribution in optoelectronic properties
- reproducibility of spin-based organic technologies

Moving towards the **miniaturisation** and **integration** of organic quantum devices

Spin Permutation Symmetry of Excited States



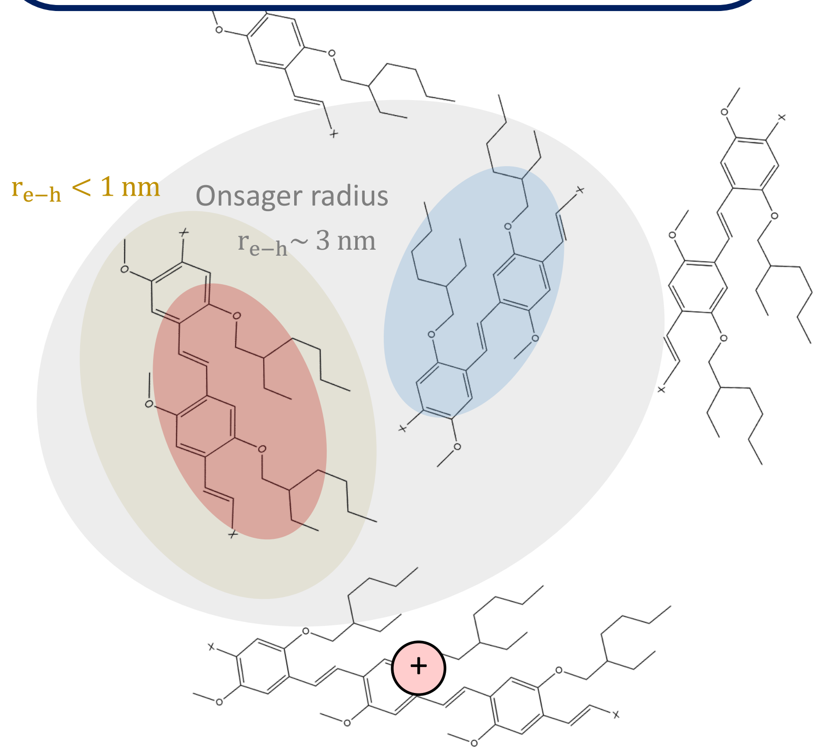
G: generation rates d: dissociation rates k: recombination rates

Excitonic Materials

Small-Molecules & Polymer Chromophores
Charge Transport: Thermally Activated Hopping

Intersystem Crossing

I. Conservation of Energy
II. Spin Flipping Mechanism



[1] M. Reuferet et al., *Nature Mater.* **4**, 340 (2005)

Singlet-Triplet Interconversion (Spin Mixing)

Traditional Fluorescent Molecules

Spin Hamiltonian: $H = H_Z + H_{ex} + H_{HF} + H_D + H_{SOC}$ [Distant Pairs]

Interactions

Zeeman: $H_Z = \frac{1}{2}\mu_B B_0[g_a \hat{\sigma}_z^a + g_b \hat{\sigma}_z^b]$

Exchange: $H_{ex} = -J\hat{S}_a \cdot \hat{S}_b$

Hyperfine: $H_{HF} = \sum_{i=1}^{2}\sum_{j=1}^{Ni}[S_i \cdot \tilde{A}_{ij} \cdot I_j]$

Dipolar: $H_D = \widehat{\boldsymbol{S}}_a^\dagger \, \widetilde{\boldsymbol{D}}_d \, \widehat{\boldsymbol{S}}_b$ $\quad (\widetilde{\boldsymbol{D}}_d)_{ab} \sim r^{-3}$

SOC: $H_{SOC} = \widehat{\boldsymbol{S}}_a^\dagger \, \widetilde{D} \, \widehat{\boldsymbol{S}}_b$ $\quad \widetilde{D} \sim Z^4$

C. Boehme & D. R. McCamey, *Organic Spintronics,* 1st Edition, pp. 257–300, (2010)

Singlet-Triplet Interconversion (Spin Mixing)

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Spin Hamiltonian: $$H = H_Z + H_{ex} + H_{HF} + H_D + H_{SOC}$$ [Distant Pairs]

<u>Interactions</u>

Zeeman: $$H_Z = \frac{1}{2}\mu_B B_0[g_a\hat{\sigma}_Z^a + g_b\hat{\sigma}_Z^b]$$

- $T_{+,-}$ splitting from hyperfine field is 0.5 μeV at 5 mT

Exchange: $$H_{ex} = -J\hat{S}_a \cdot \hat{S}_b$$

- Dictates size where spin-dept. transitions occur
- Pair distance r ~ 3 nm → small ψ overlap

Hyperfine: $$H_{HF} = \sum_{i=1}^{2}\sum_{j=1}^{Ni}[S_i \cdot \tilde{A}_{ij} \cdot I_j]$$

DOMINANT – responsible for *intrinsic* MFEs in OSCs

Dipolar: $$H_D = \hat{\boldsymbol{S}}_a^\dagger \, \widetilde{\boldsymbol{D}}_d \, \hat{\boldsymbol{S}}_b \qquad (\widetilde{\boldsymbol{D}}_d)_{ab} \sim r^{-3}$$

- Negligible at large e-h separation distances / USMEL
- Outcompeted by exchange at short distances

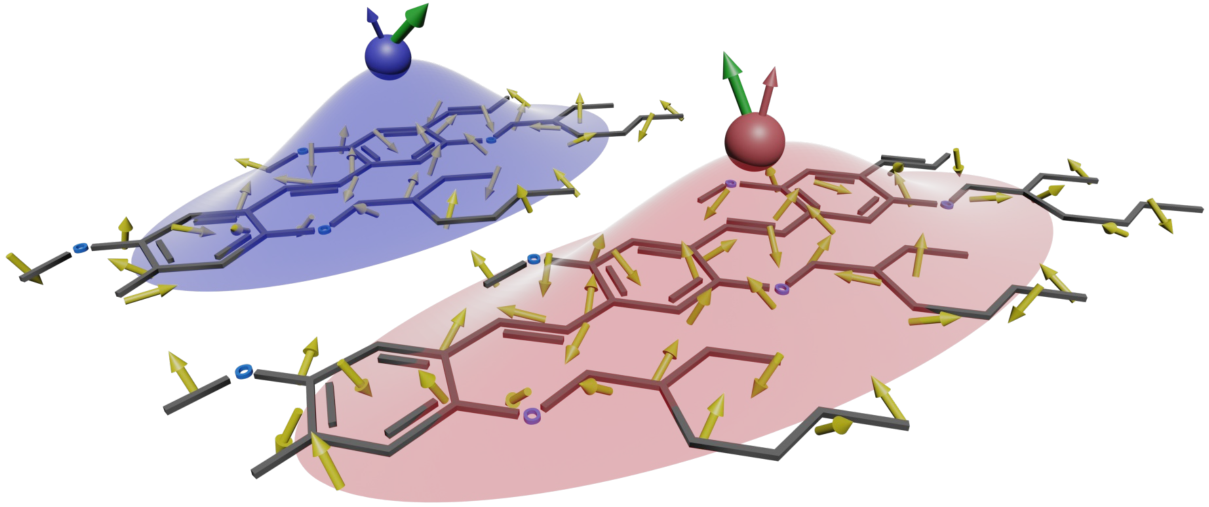
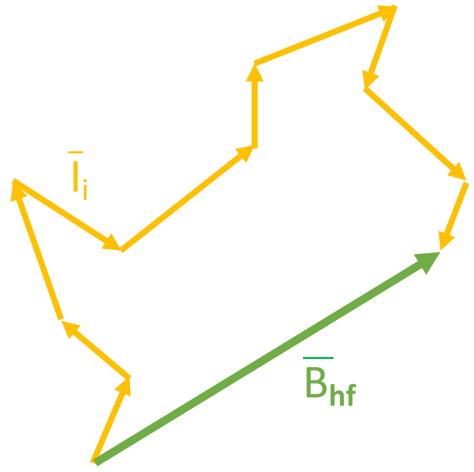
SOC: $$H_{SOC} = \hat{\boldsymbol{S}}_a^\dagger \, \widetilde{D} \, \hat{\boldsymbol{S}}_b \qquad \widetilde{D} \sim Z^4$$

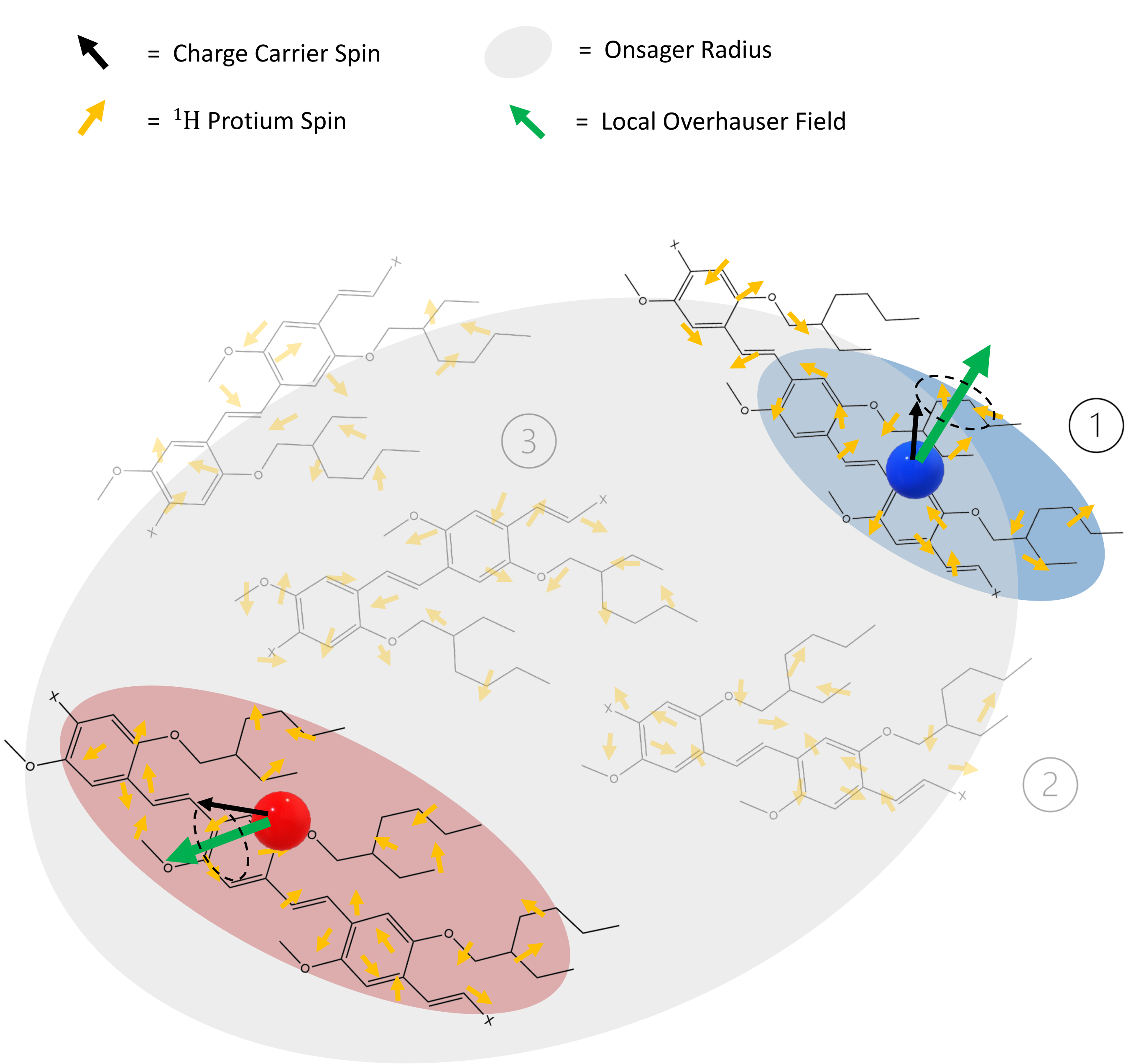
- Weak due to hydrocarbon composition

C. Boehme & D. R. McCamey, *Organic Spintronics,* 1st Edition, pp. 257–300, (2010)

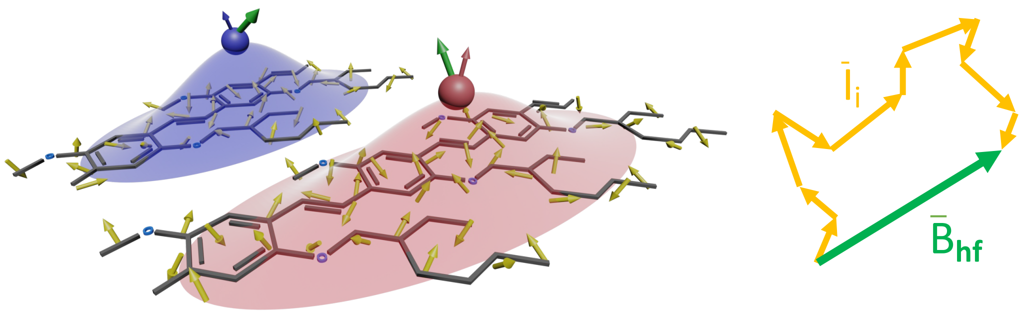
The Hyperfine Interaction

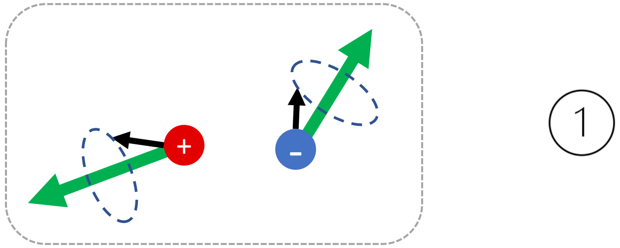
$$H_{hf} = \sum_k a_{HF,k}\ \mathbf{S} \cdot \mathbf{I_k}\ |\boldsymbol{\psi}(\mathbf{r_k})|^2$$

Interaction	Property
	

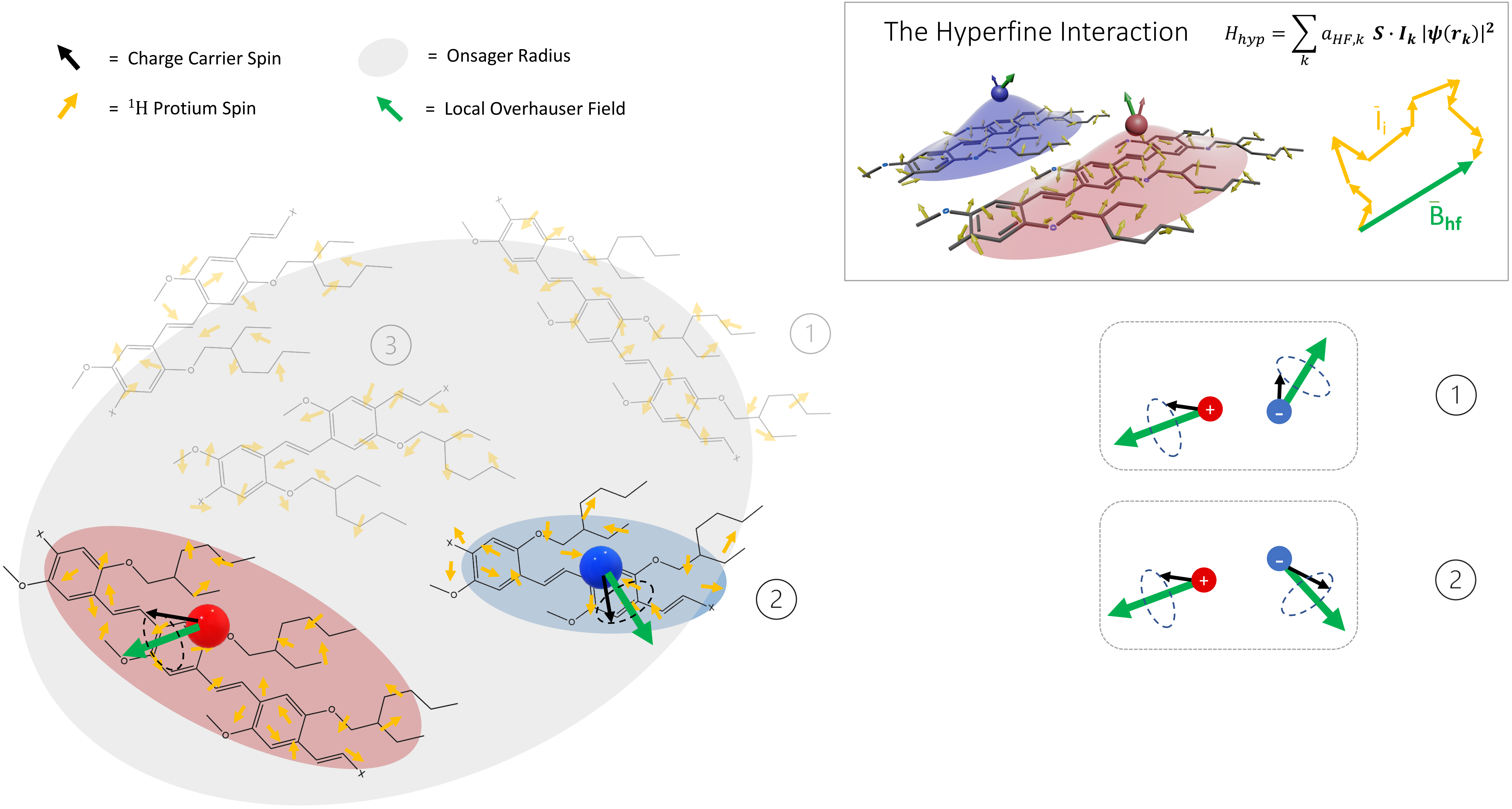


The Hyperfine Interaction $H_{hyp} = \sum_k a_{HF,k}\, \boldsymbol{S} \cdot \boldsymbol{I_k}\, |\boldsymbol{\psi}(\boldsymbol{r_k})|^2$

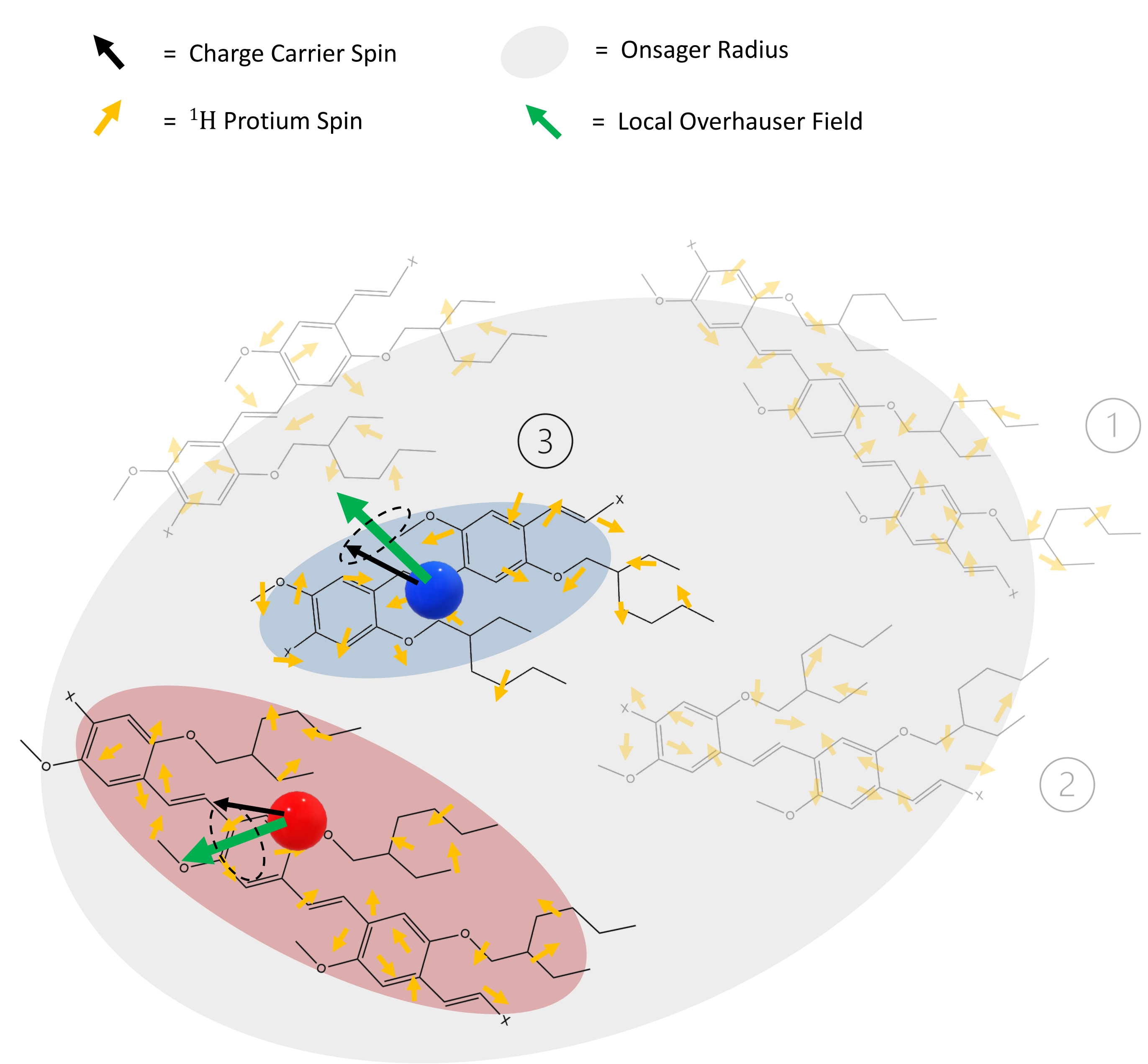


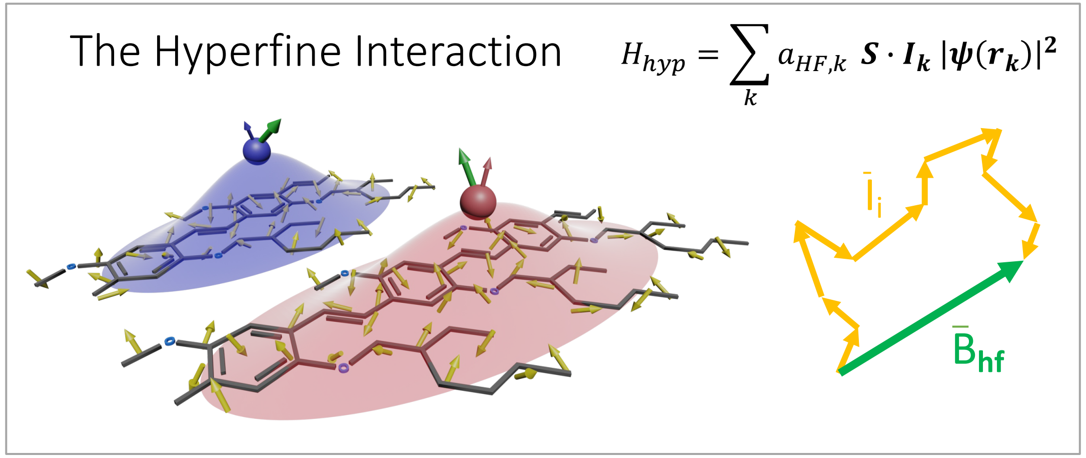


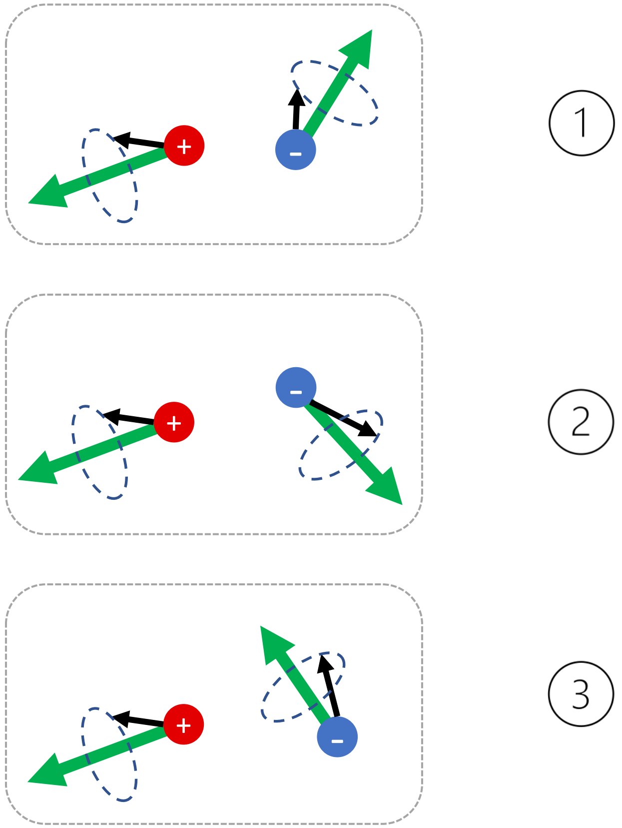
W. Baker, K. Ambal, D. Waters *et al.*, *Nat Commun* **3,** 898 (2012)



W. Baker, K. Ambal, D. Waters *et al.*, *Nat Commun* **3,** 898 (2012)





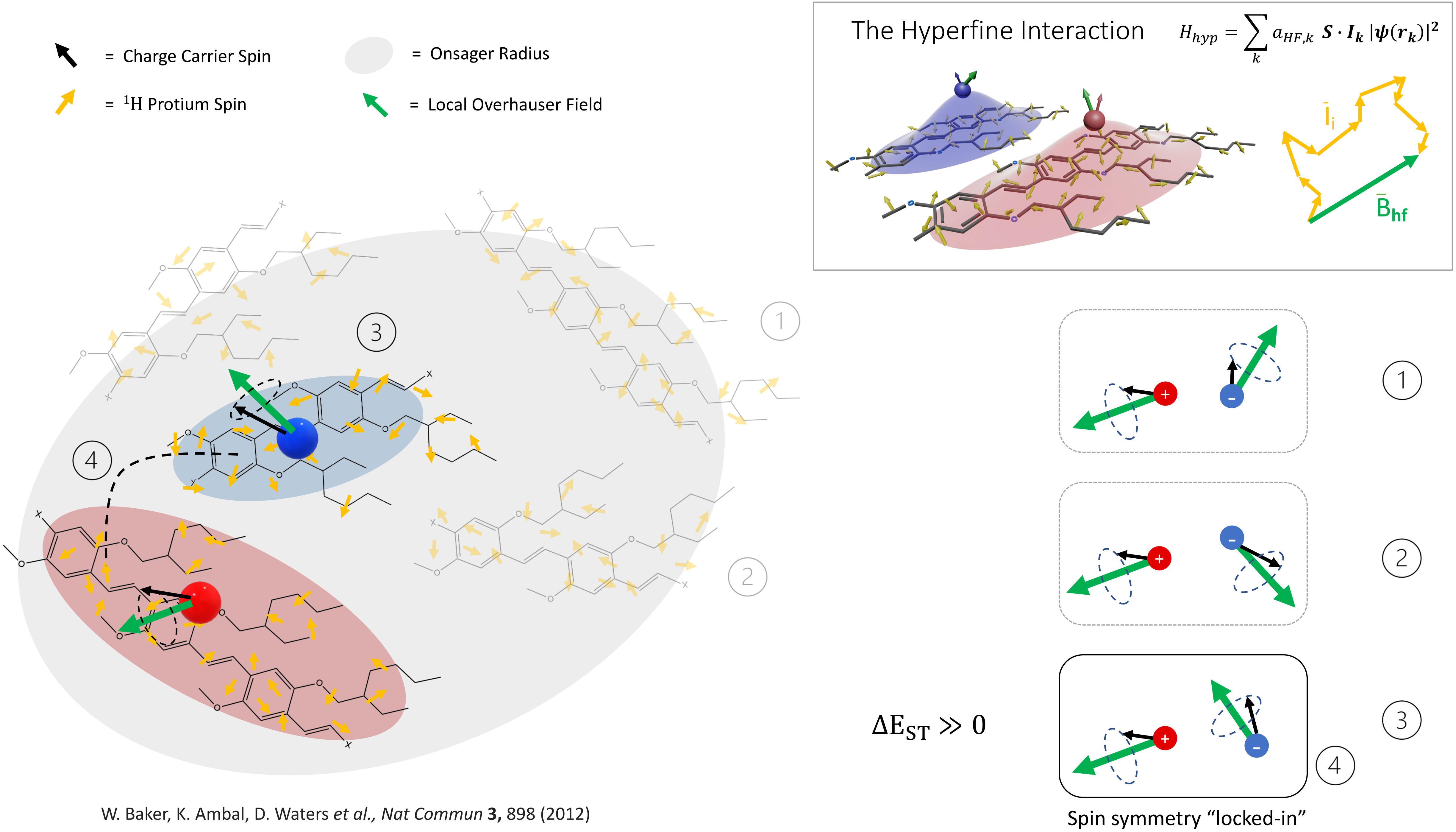


Spin mixing

$\Delta\omega_{hf} + \Delta\theta$

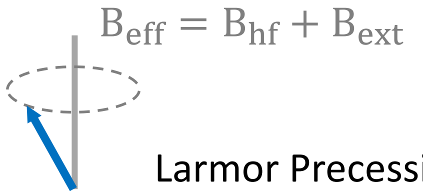
mixed state: $\alpha|T_0\rangle + \beta|S\rangle$

W. Baker, K. Ambal, D. Waters *et al.*, *Nat Commun* **3**, 898 (2012)

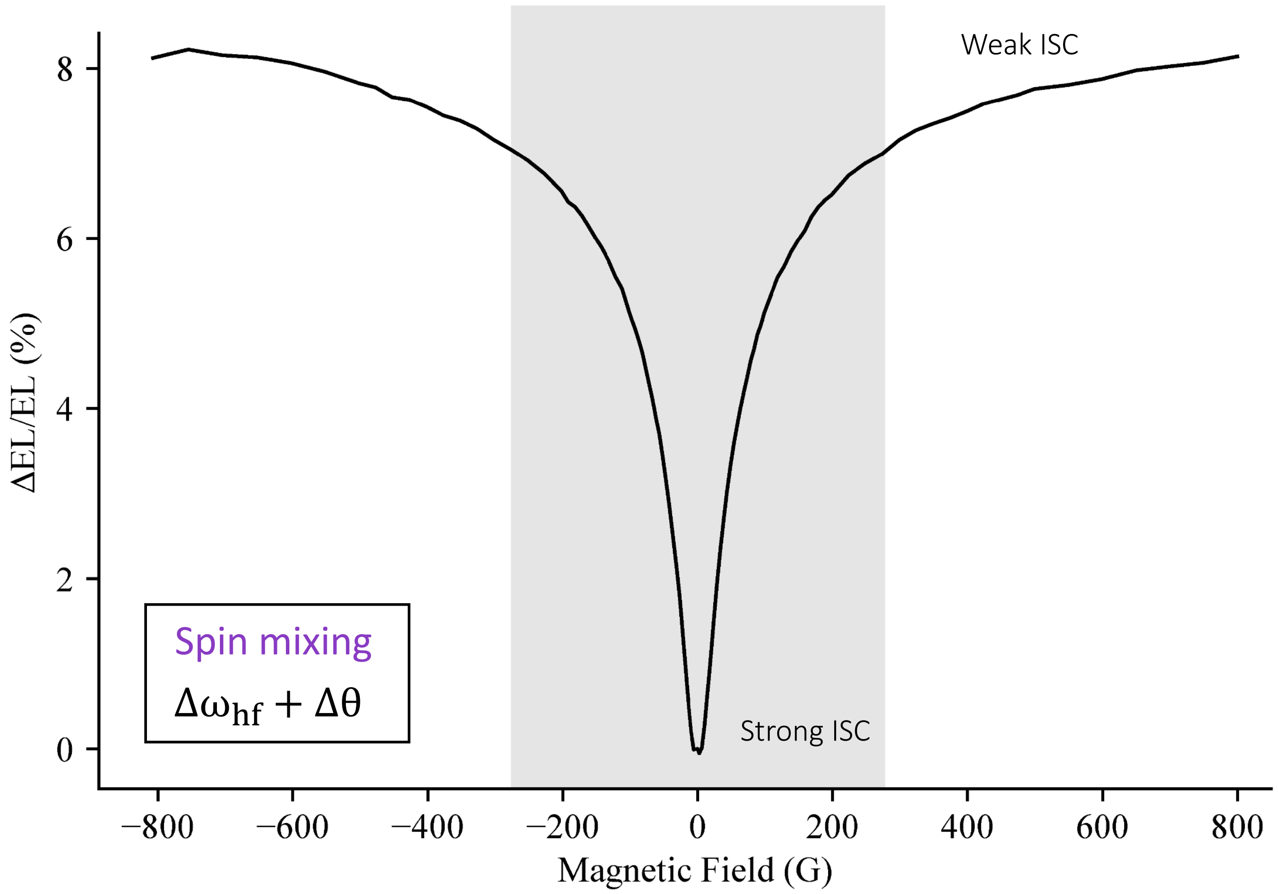


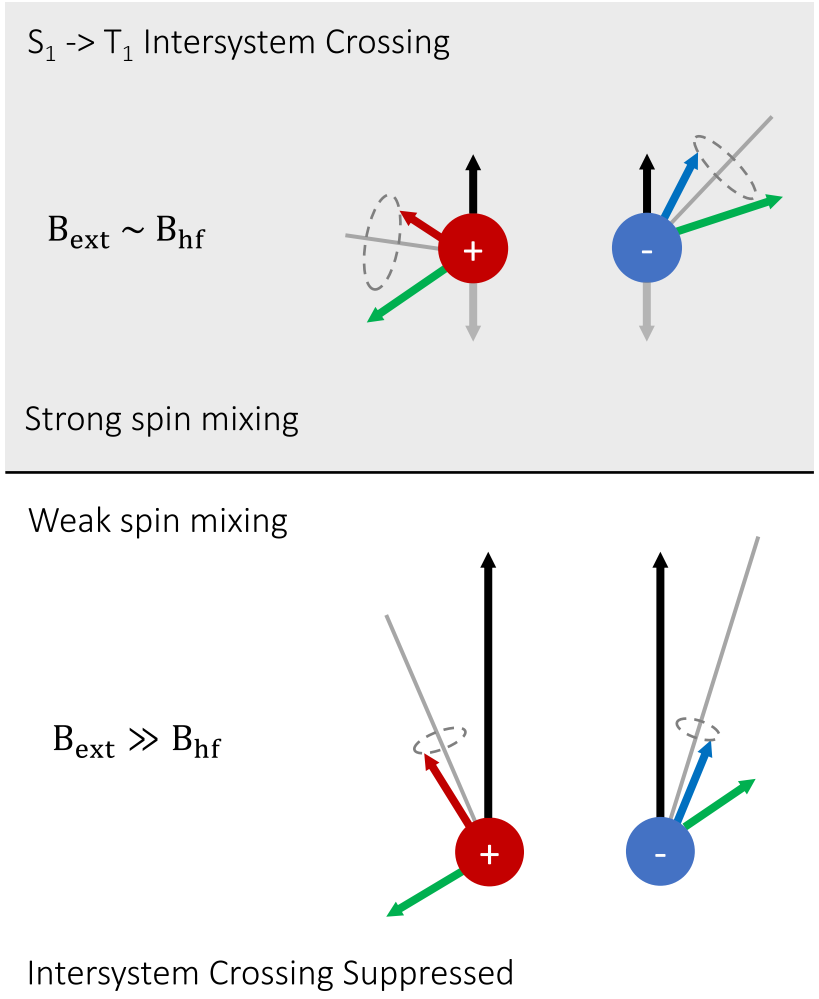
W. Baker, K. Ambal, D. Waters *et al.*, *Nat Commun* **3**, 898 (2012)

Probing Hyperfine Fields using Magnetic Fields



Magnetoelectroluminescence (MEL)

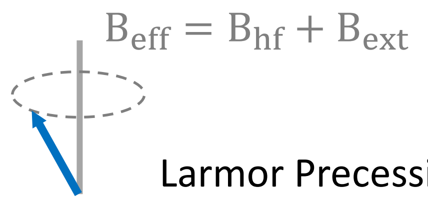


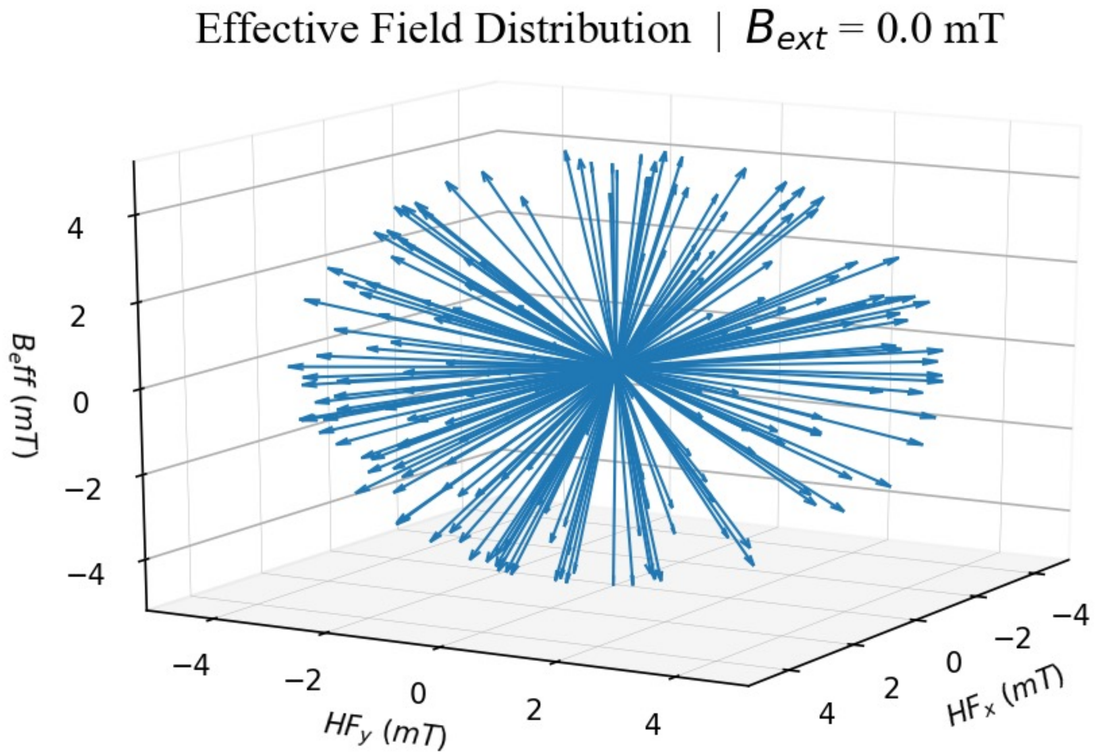


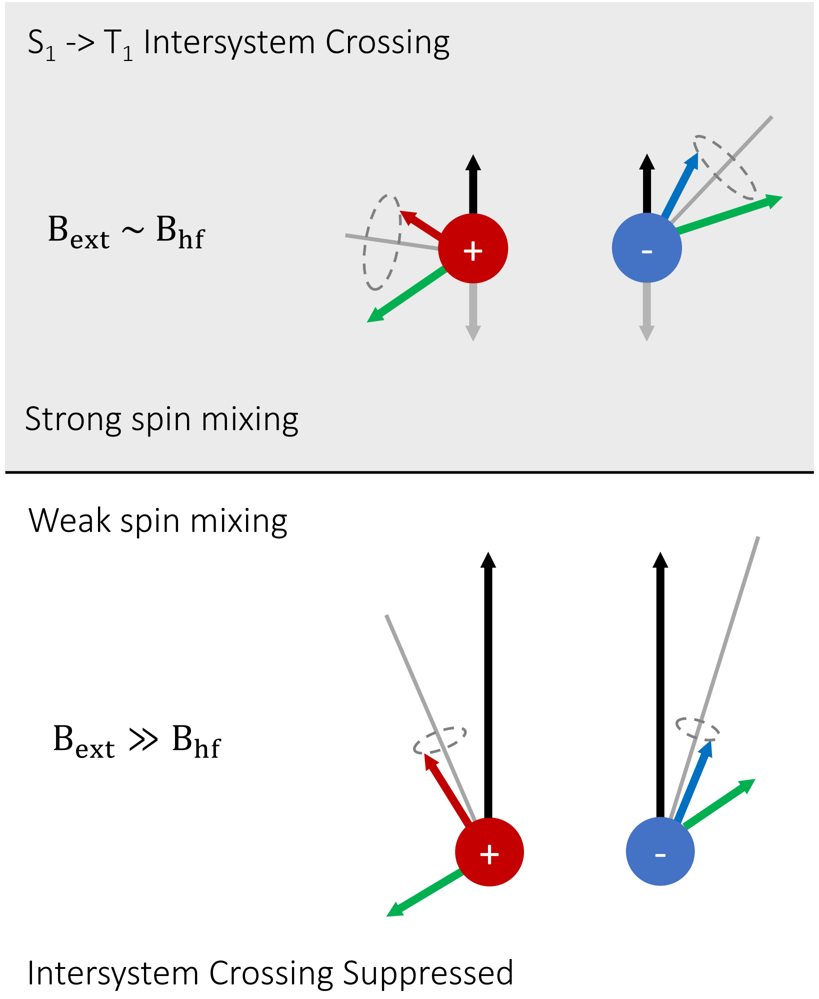
Spin mixing

$\Delta\omega_{hf} + \Delta\theta$

Overcoming Random Hyperfine Fields



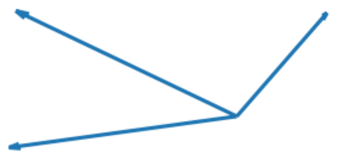


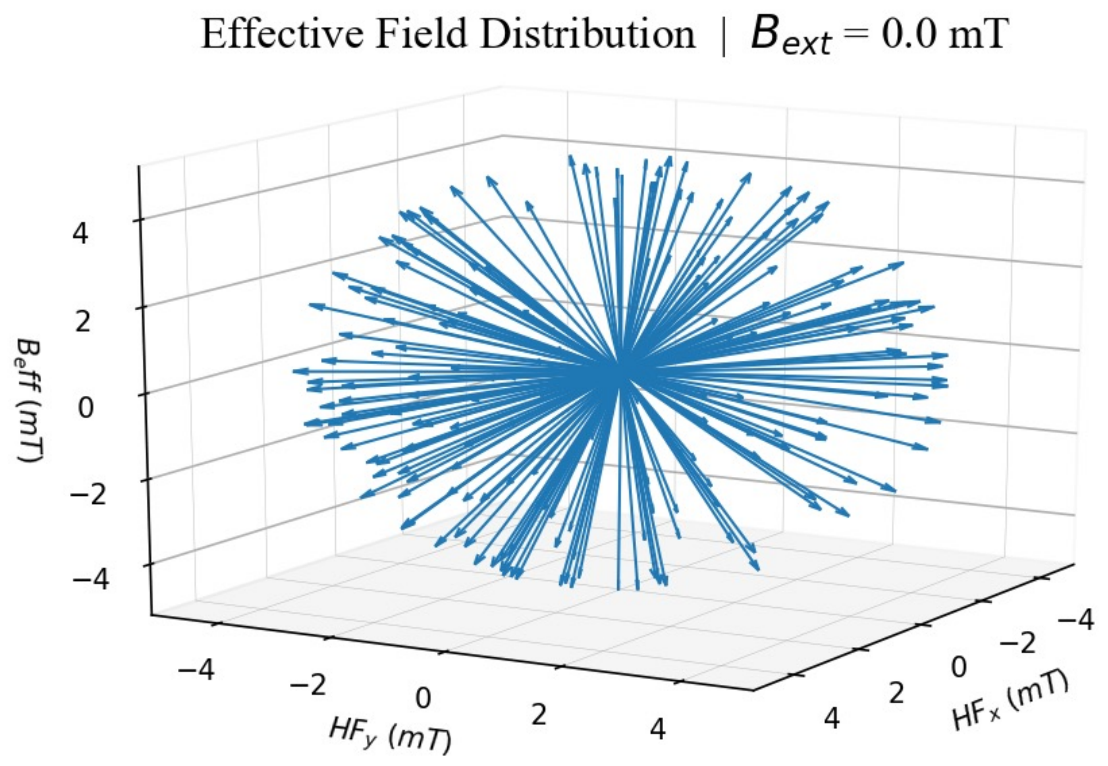


Spin mixing

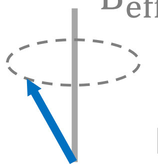
$\Delta\omega_{hf} + \Delta\theta$

Overcoming Random Hyperfine Fields





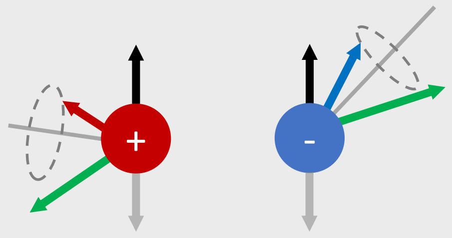
$B_{eff} = B_{hf} + B_{ext}$



Larmor Precession

S_1 -> T_1 Intersystem Crossing

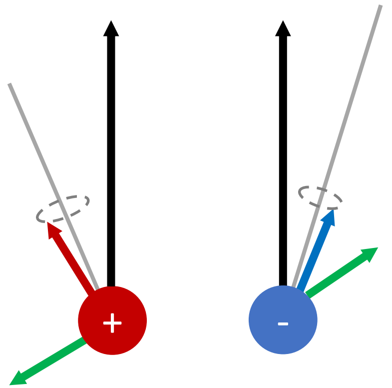
$B_{ext} \sim B_{hf}$



Strong spin mixing

Weak spin mixing

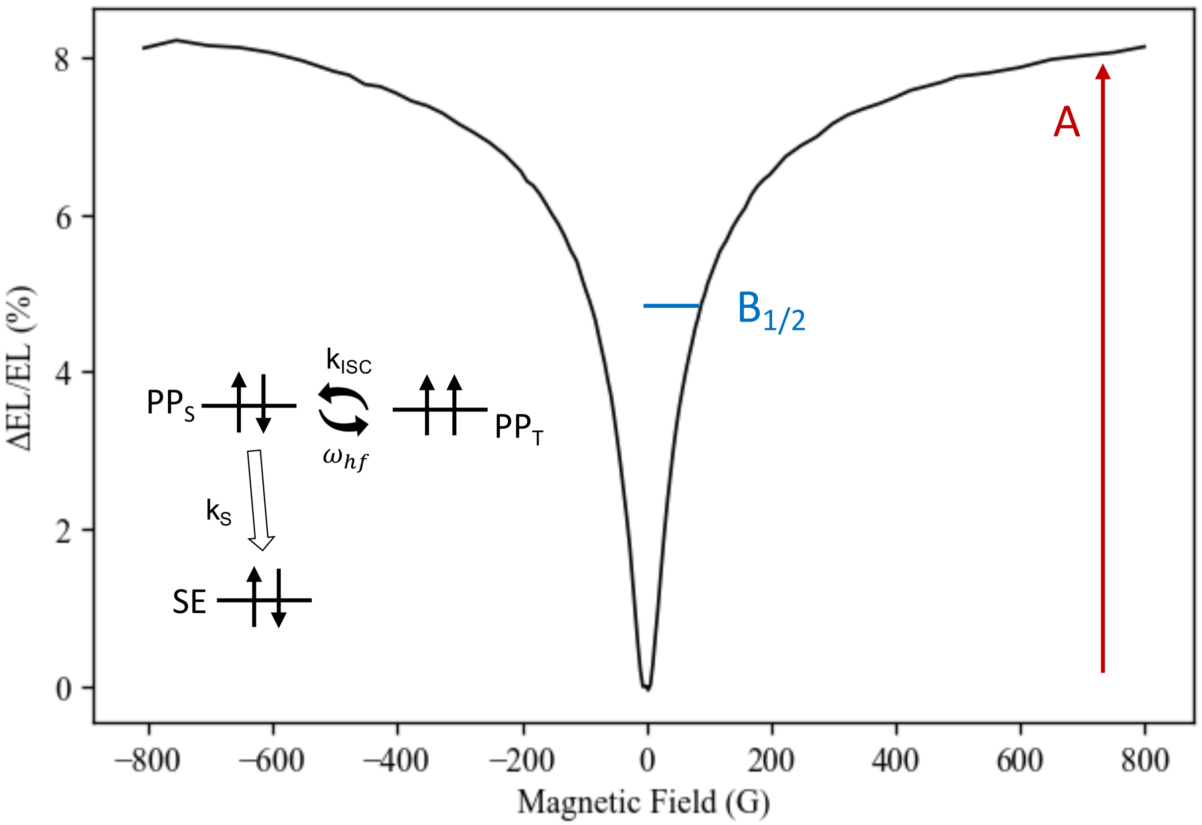
$B_{ext} \gg B_{hf}$



Intersystem Crossing Suppressed

Fitting parameters A and $B_{1/2}$ of the MEL curve give information about spin properties

$$\mathrm{MEL(B)} = \mathrm{A}\frac{\mathrm{B}^2}{(|\mathrm{B}| + \mathrm{B}_0)^2} + \delta$$



S.P. Kersten, A.J. Schellekens, B. Koopmans, P. A. Bobbert, *PRL*, 106 (19), 197402 (2011)

T.D. Nguyen *et al.*, *Nature Mater* **9,** 345–352 (2010)

Amplitude (A)

A competition between **spin mixing** (ω_{hf}) and **singlet exciton formation rate** (k_S)

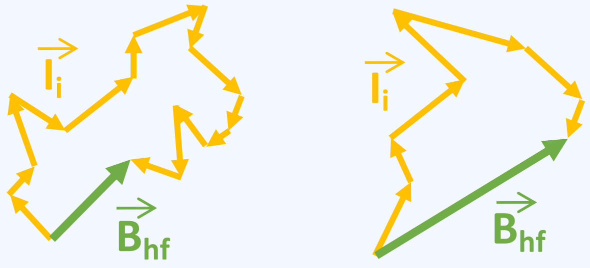
- Large **A** => $k_S / \omega_{hf} \ll 1$
- Small **A** => $k_S / \omega_{hf} \gg 1$

k_s depends on material properties

Half-Width ($B_{1/2}$)

A measure of the **hyperfine interaction**

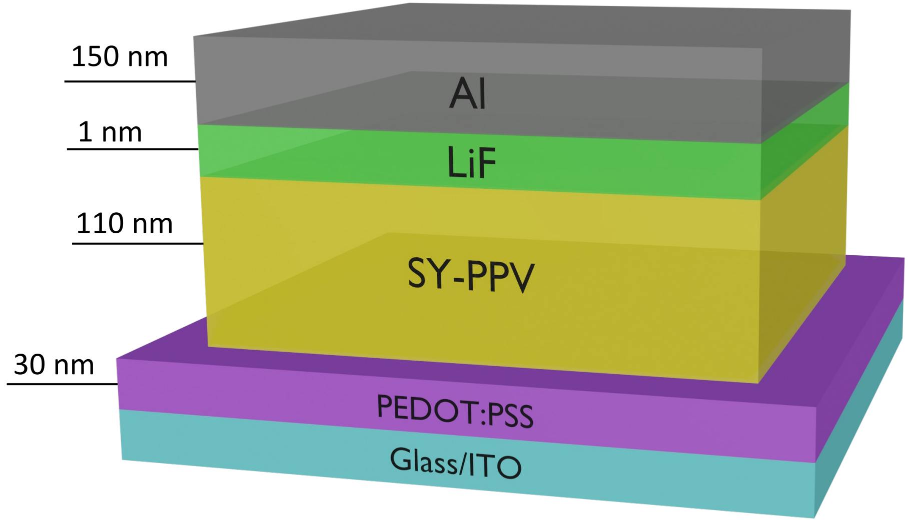
- **characteristic volume** of polarons (CLT)

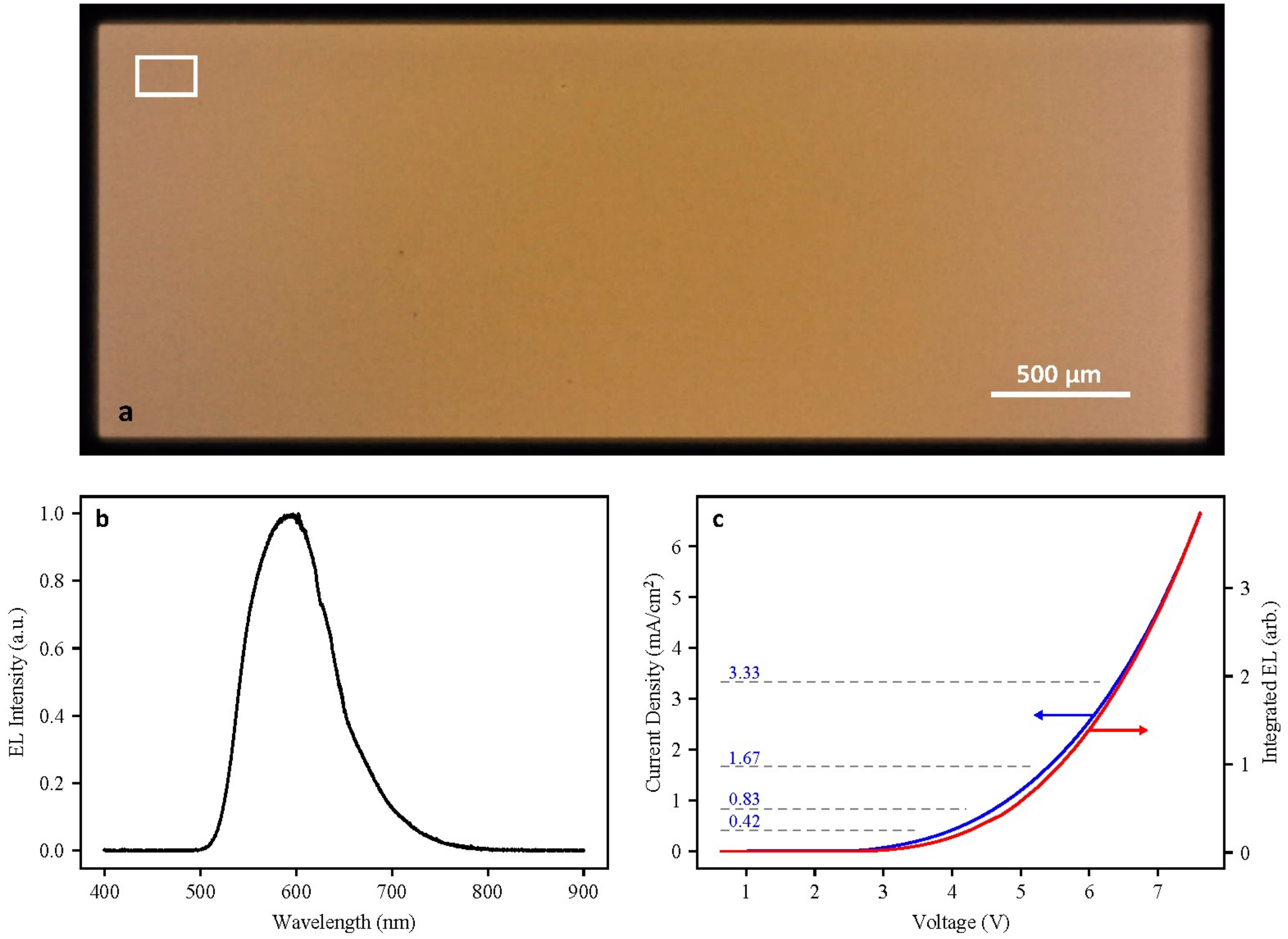


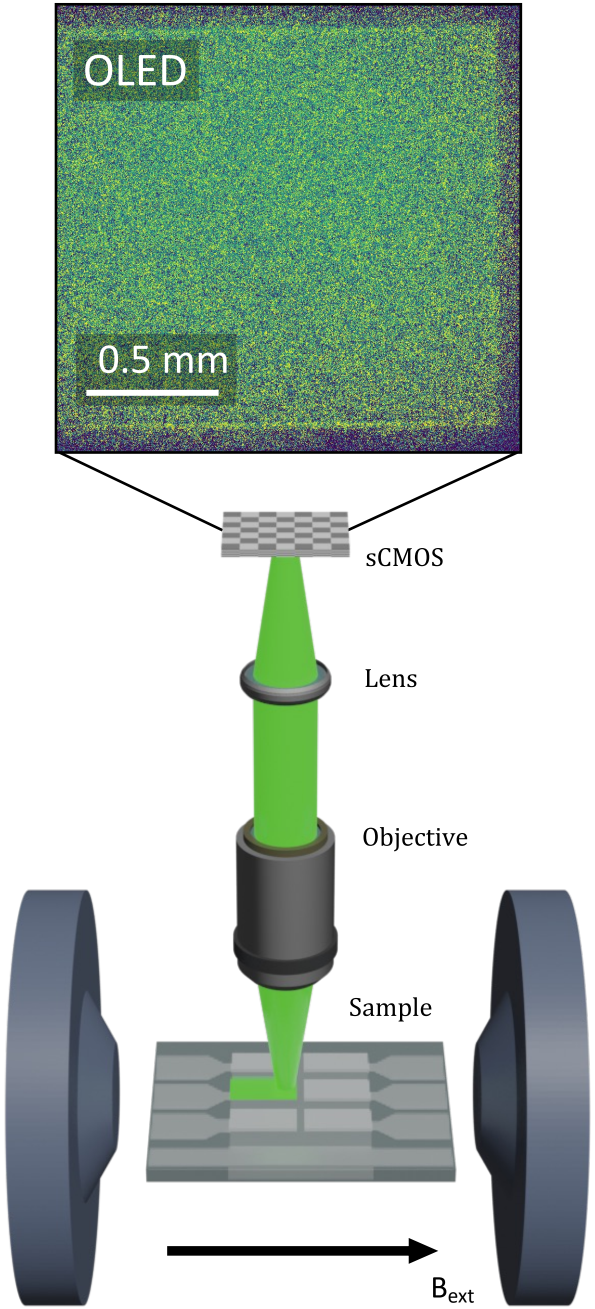
$$\mathbf{B}_{\mathrm{hf}} \sim 1/\sqrt{\mathrm{N}} \sim 1/\sqrt{\mathrm{V}}$$

Probing the **quantum properties** of materials in organic electronics

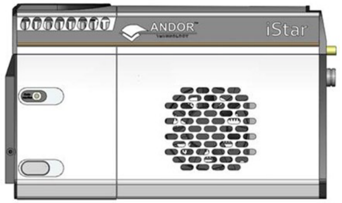
Simple vertical structure polymer OLED

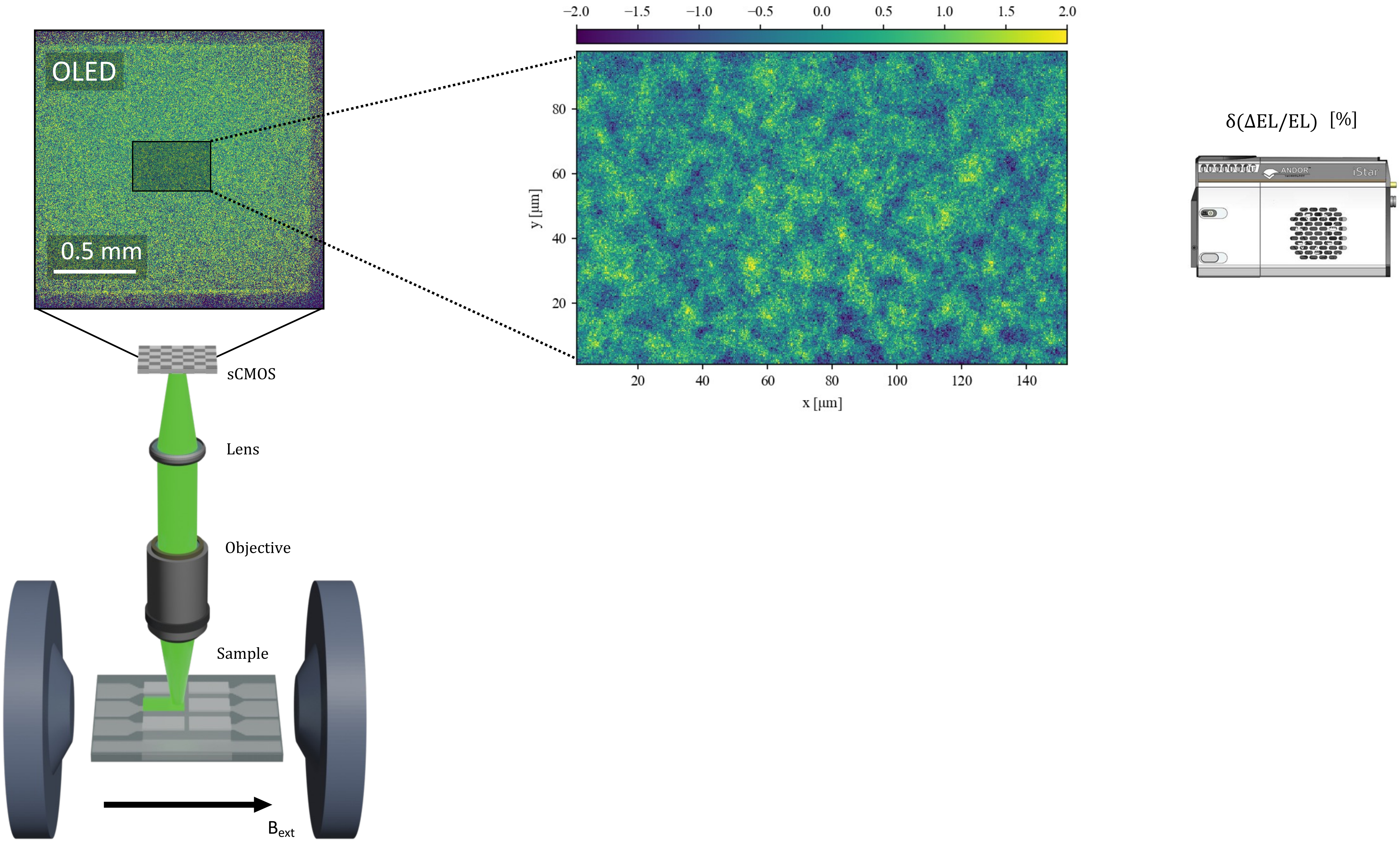


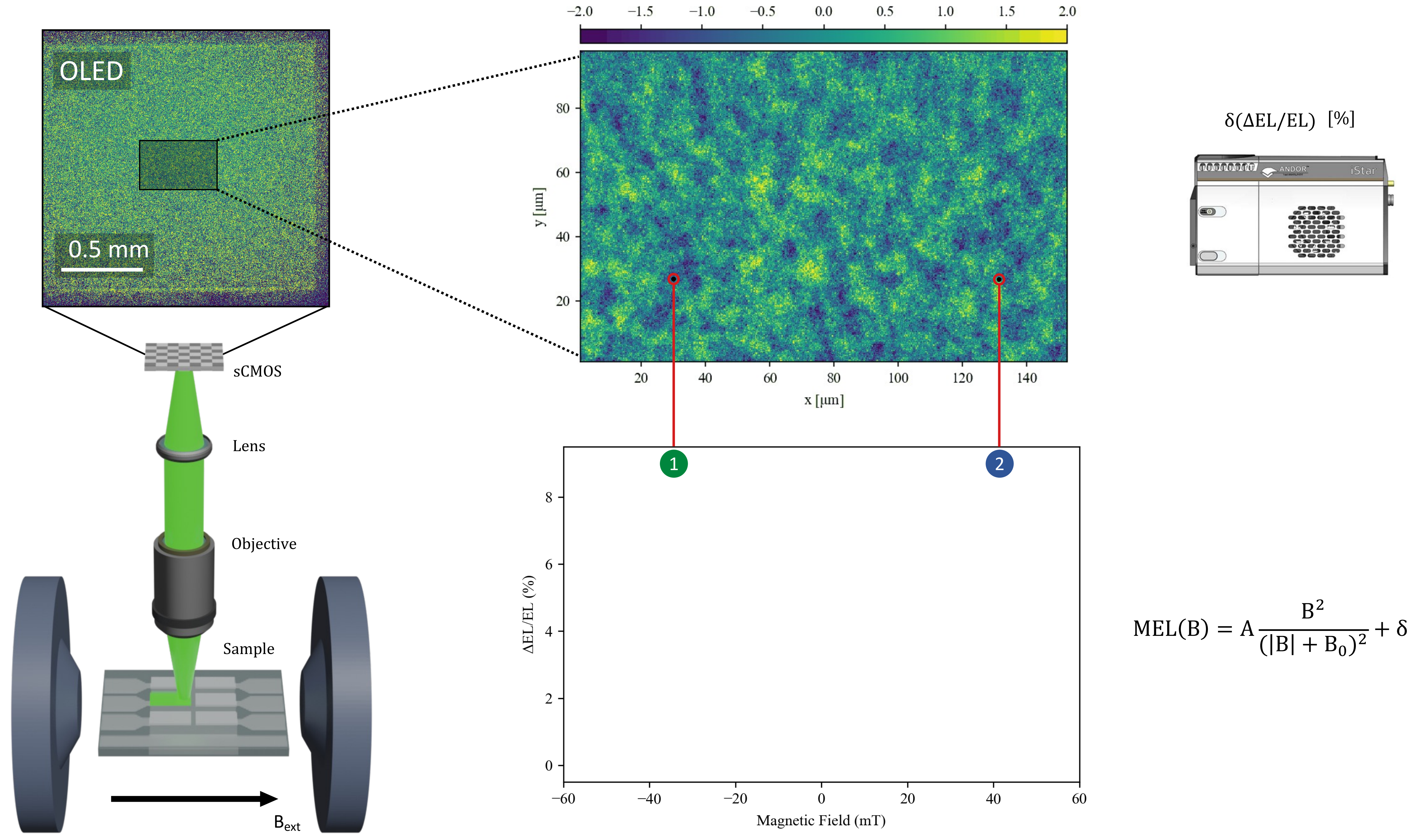




δ(ΔEL/EL) [%]

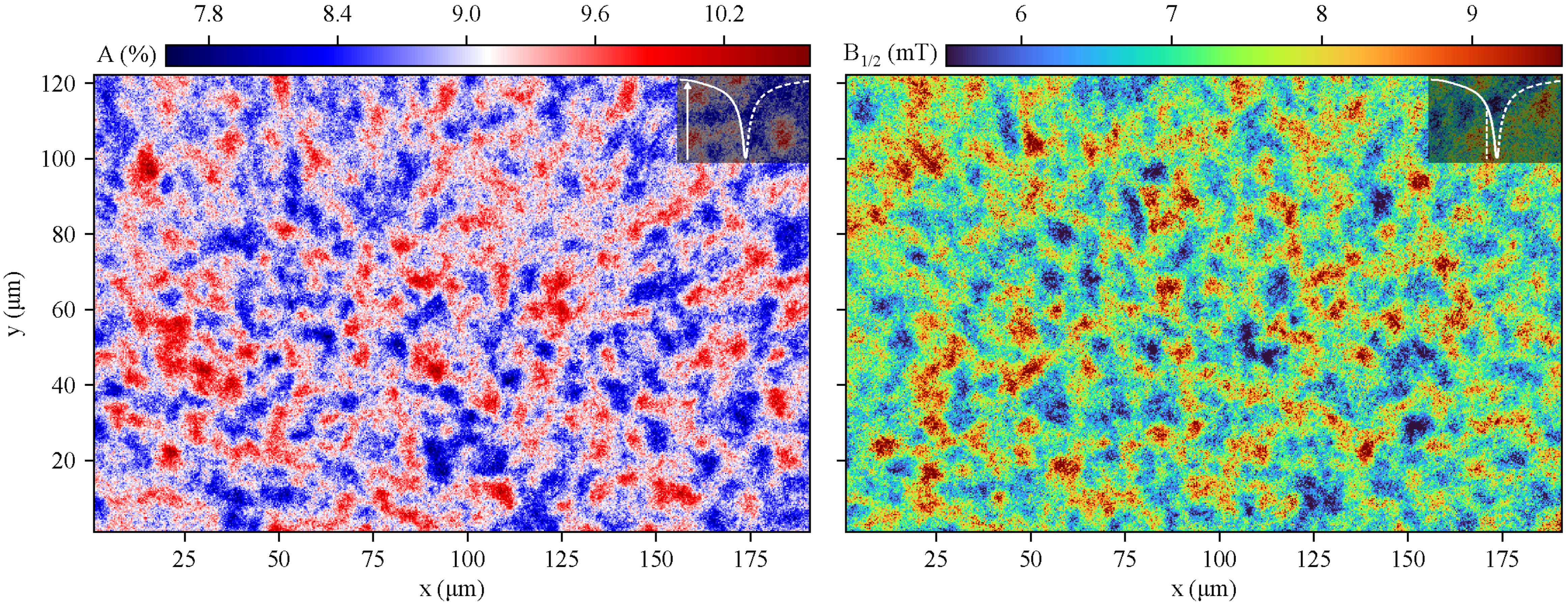



OLED
0.5 mm
sCMOS
Lens
Objective
Sample
B_ext
−2.0
−1.5
−1.0
−0.5
0.0
0.5
1.0
1.5
2.0
y [µm]
x [µm]
δ(ΔEL/EL) [%]
ANDOR
iStar



OLED
0.5 mm
sCMOS
Lens
Objective
Sample
B_{ext}
−2.0 −1.5 −1.0 −0.5 0.0 0.5 1.0 1.5 2.0
y [µm]
x [µm]
1
2
ΔEL/EL (%)
Magnetic Field (mT)
δ(ΔEL/EL) [%]
ANDOR
iStar
$$\mathrm{MEL}(B) = A\frac{B^2}{(|B| + B_0)^2} + \delta$$

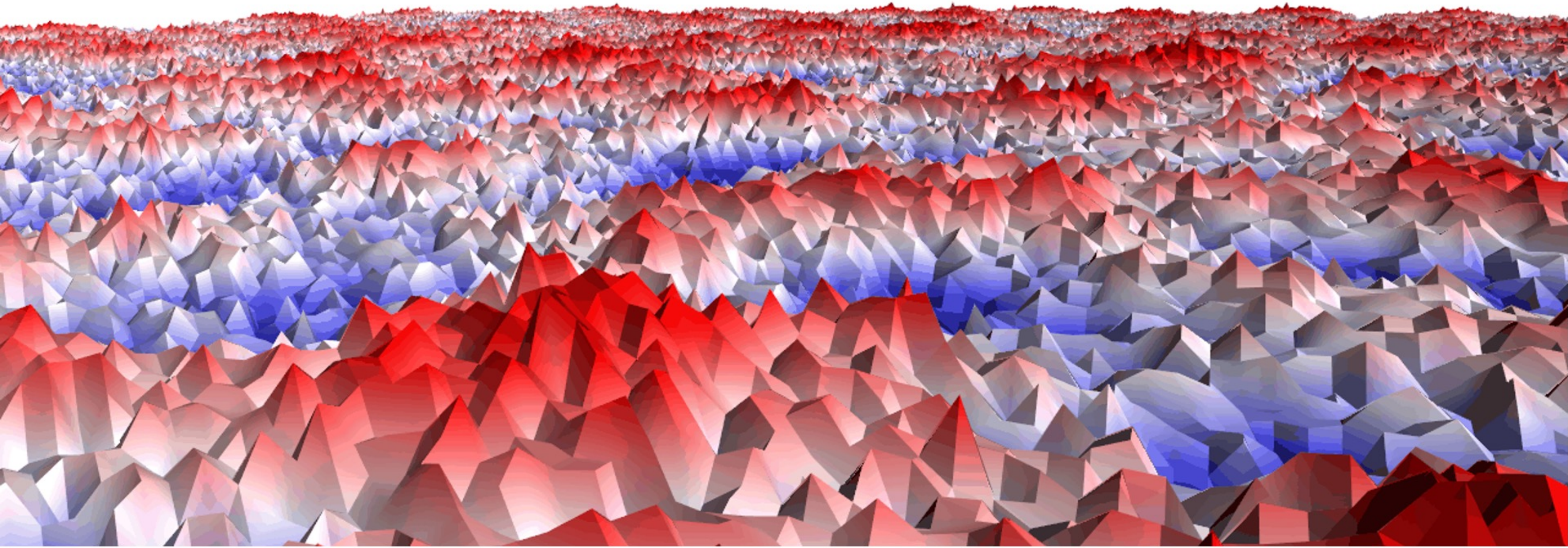
Spatial distributions of MEL parameters (A, $B_{1/2}$)



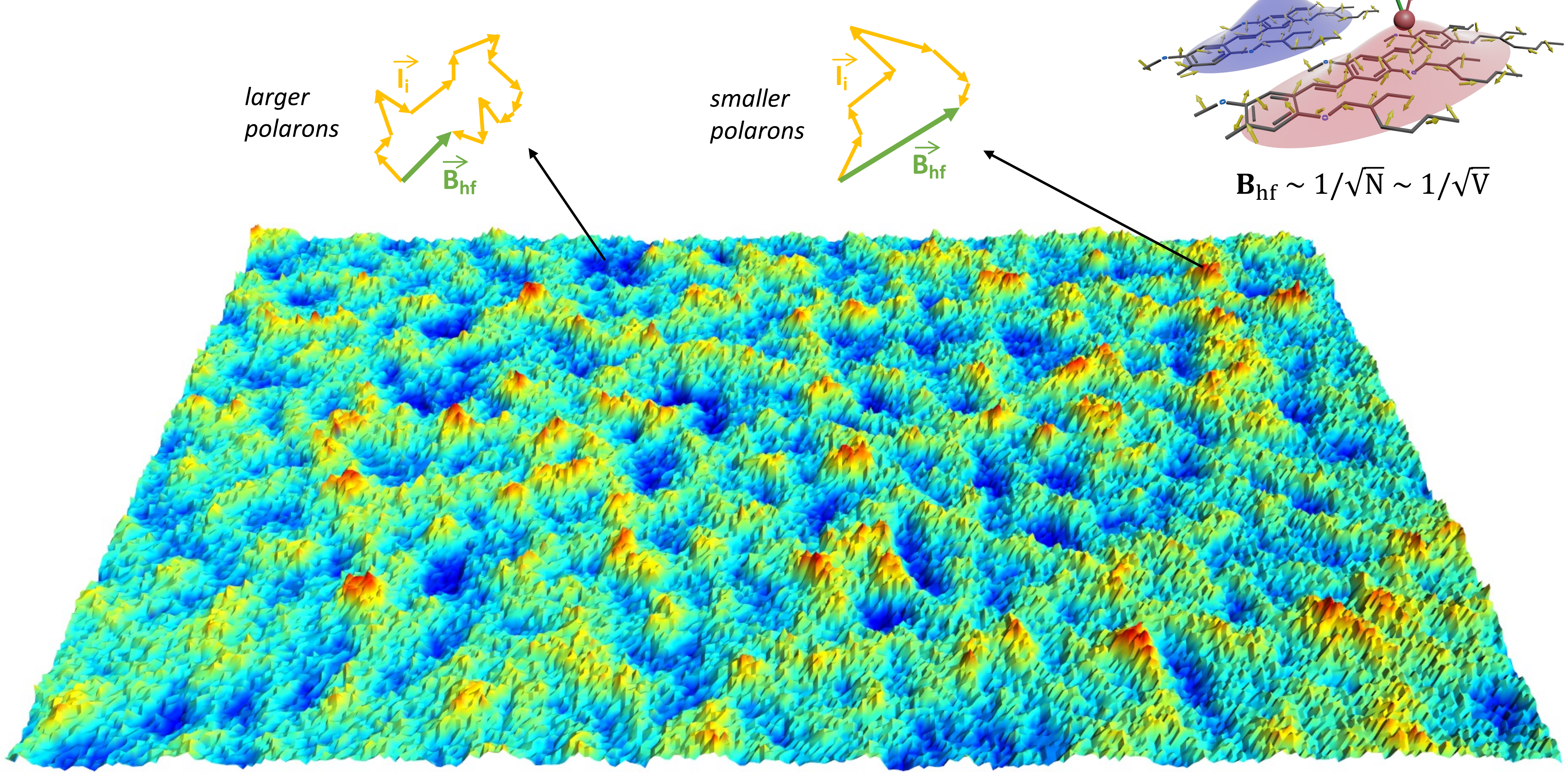
A competition between **spin mixing** (ω_{hf}) and **singlet exciton formation rate** (k_S)…

regions of larger **A** => $k_S / \omega_{hf} \ll 1$

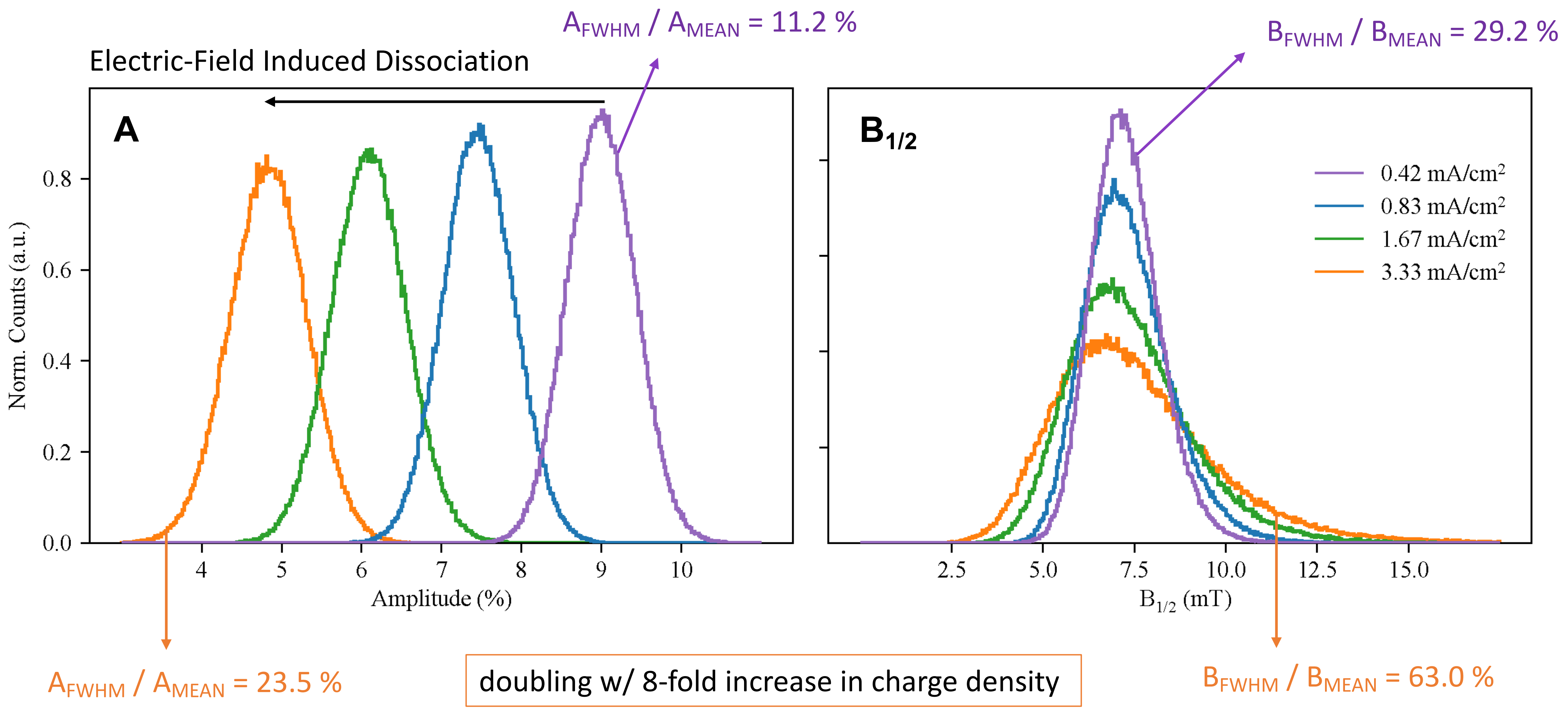
smaller **A** => $k_S / \omega_{hf} \gg 1$



A measure of the **hyperfine interaction** and therefore **characteristic volume** of polarons …

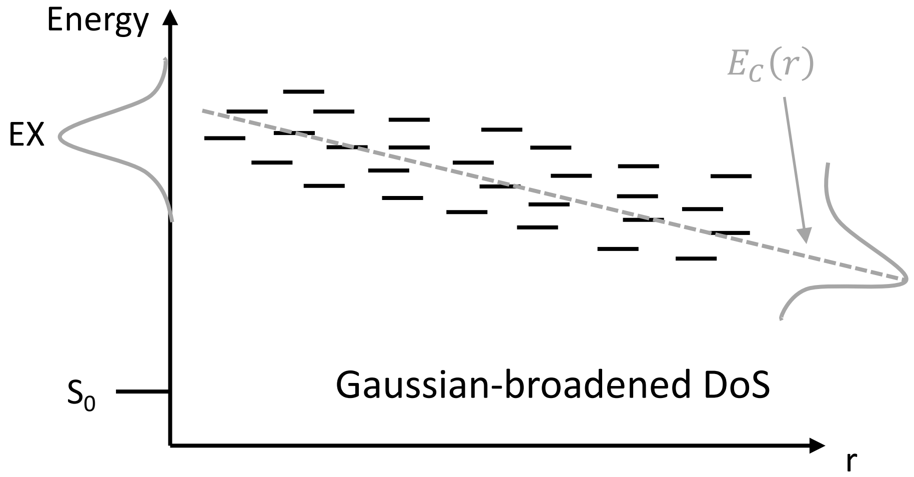


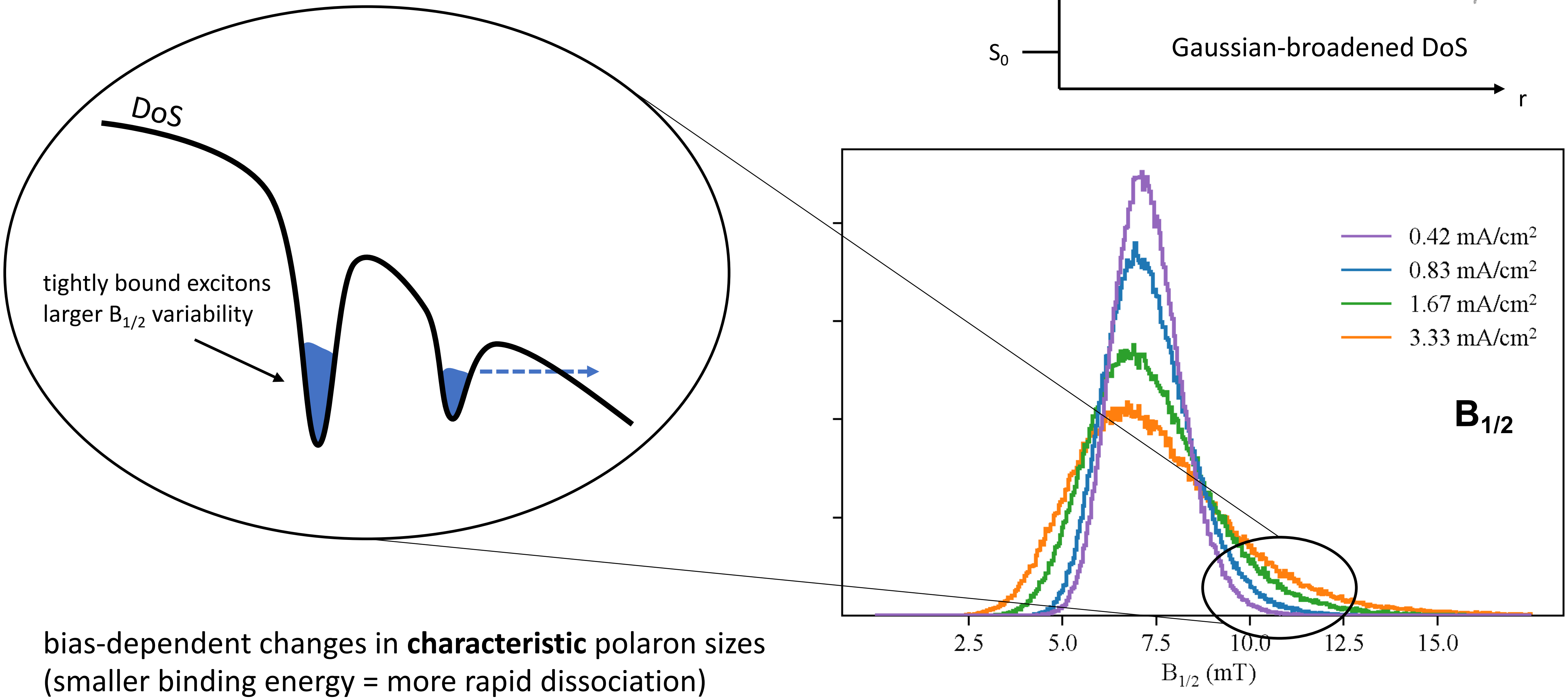
Intra-device **variation** of MEL parameters (A, $B_{1/2}$)



Electric-Field Induced Dissociation

$$E_C(r) = -\frac{e^2}{4\pi\varepsilon_0\varepsilon r} - eF.r$$



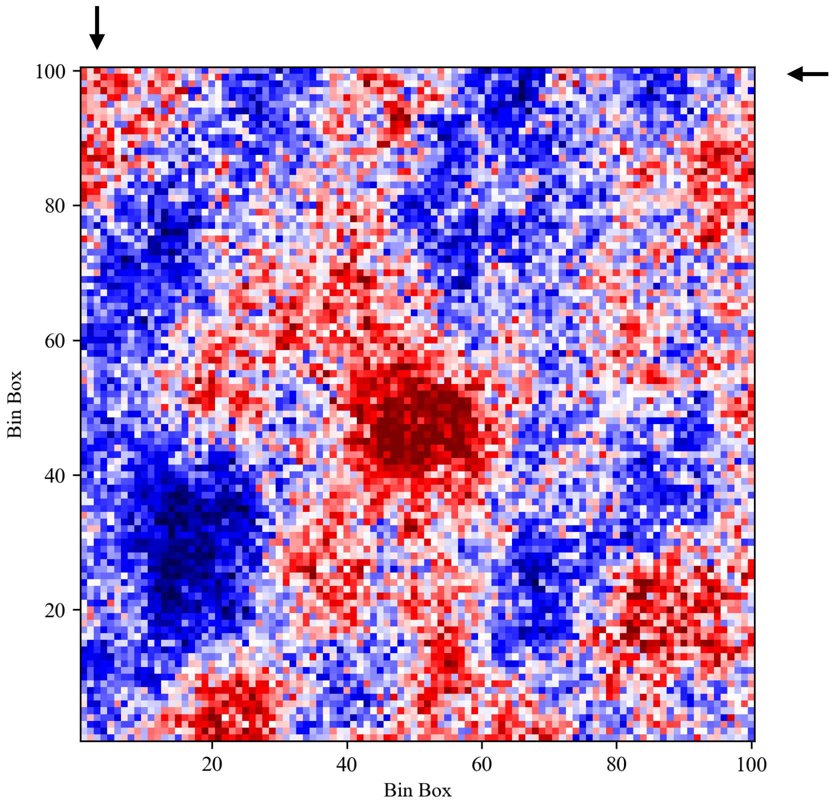


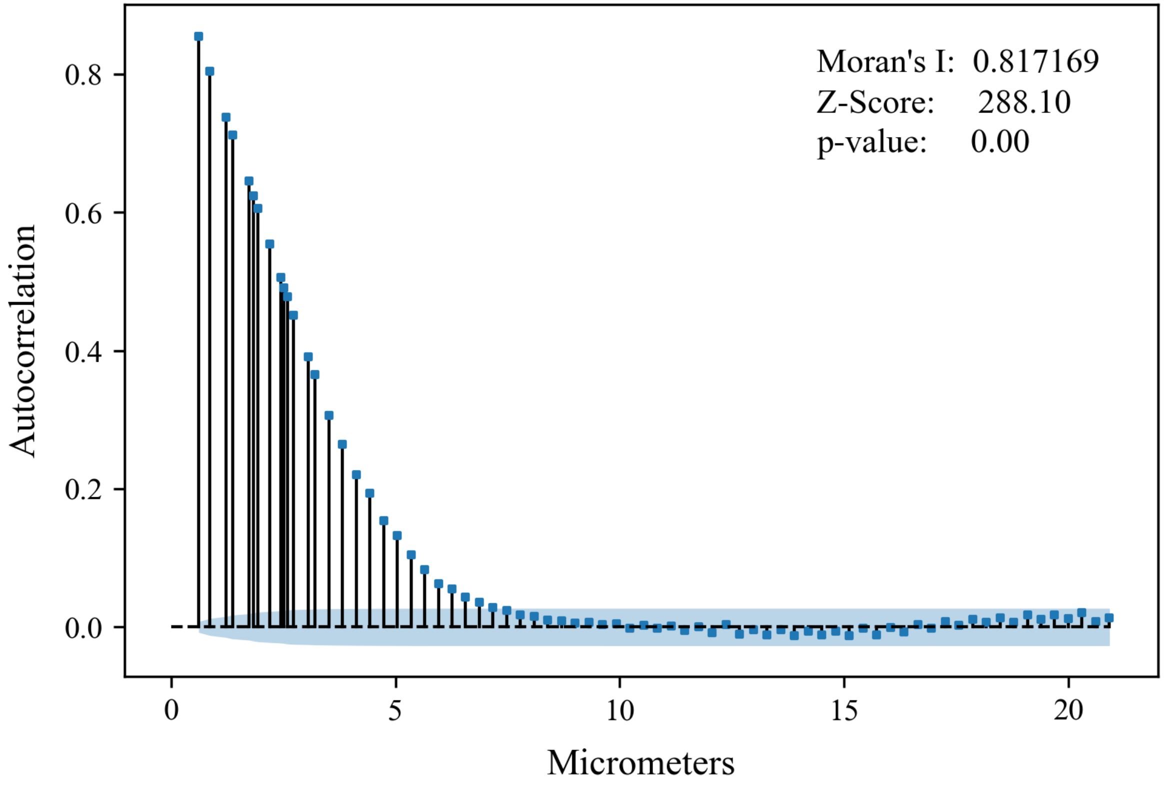
bias-dependent changes in **characteristic** polaron sizes
(smaller binding energy = more rapid dissociation)

Moran's I – A global measure of **spatial autocorrelation**

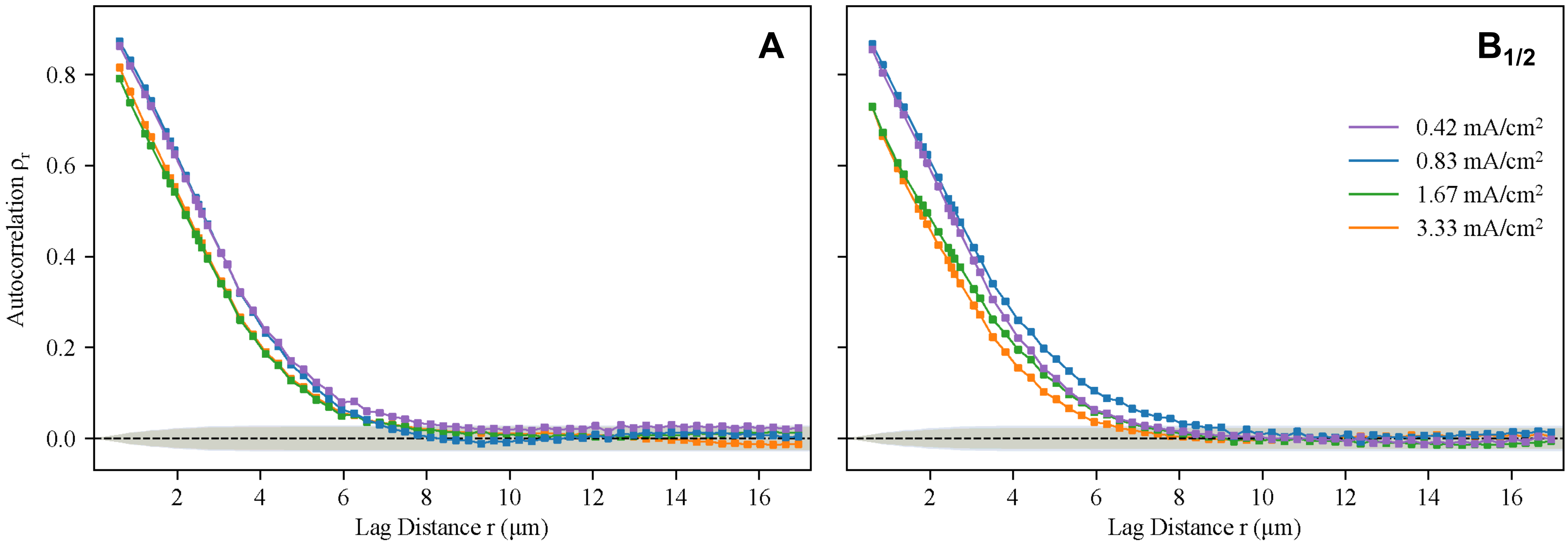
Calculating the similarity of values between neighbours:

$$\rho_r = \frac{\gamma_r}{\gamma_0} = \frac{\sum_i^M \sum_j^N \sigma_{ij} \sum_k^M \sum_l^N w_{kl} \cdot \sigma_{kl}}{\sum_i^M \sum_j^N {\sigma_{ij}}^2}$$

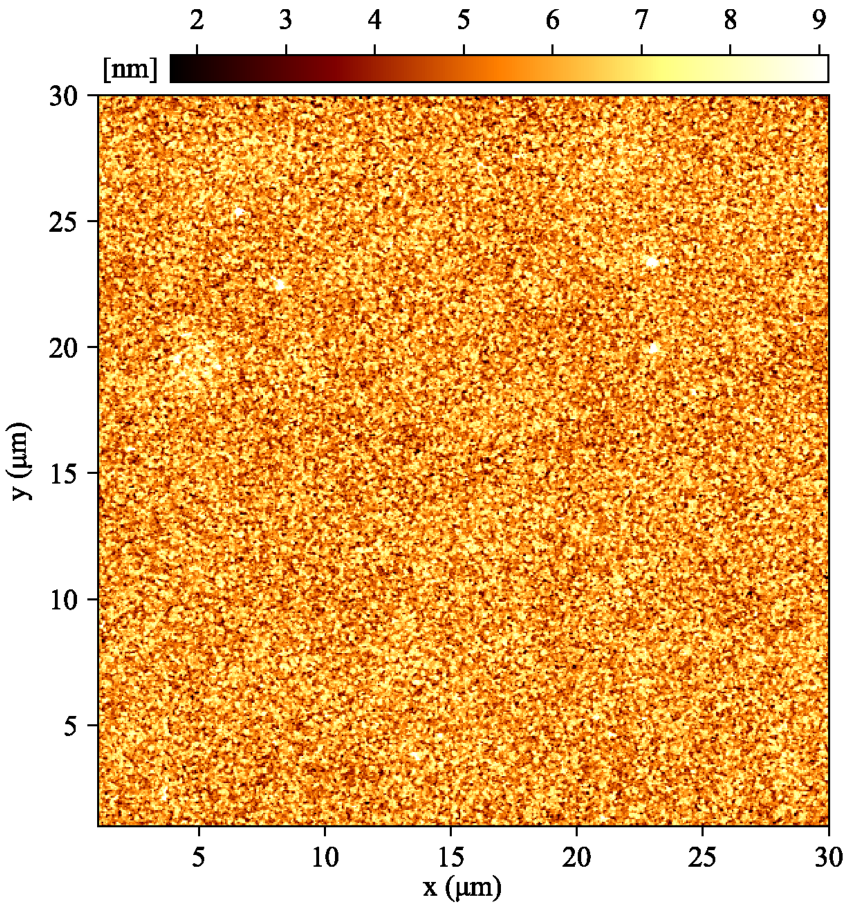




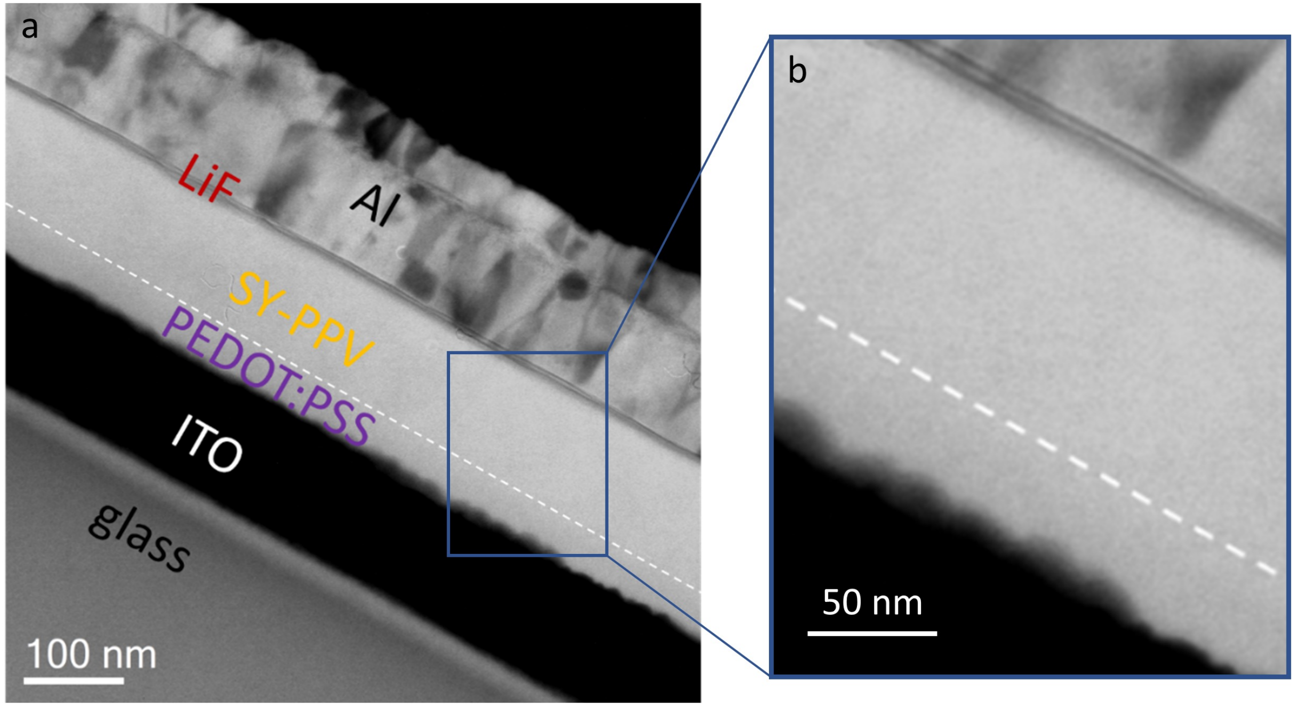
Spatial correlation of MEL parameters (A, $B_{1/2}$)



Film Homogeneity – Uniform and defect free on a microscopic scale

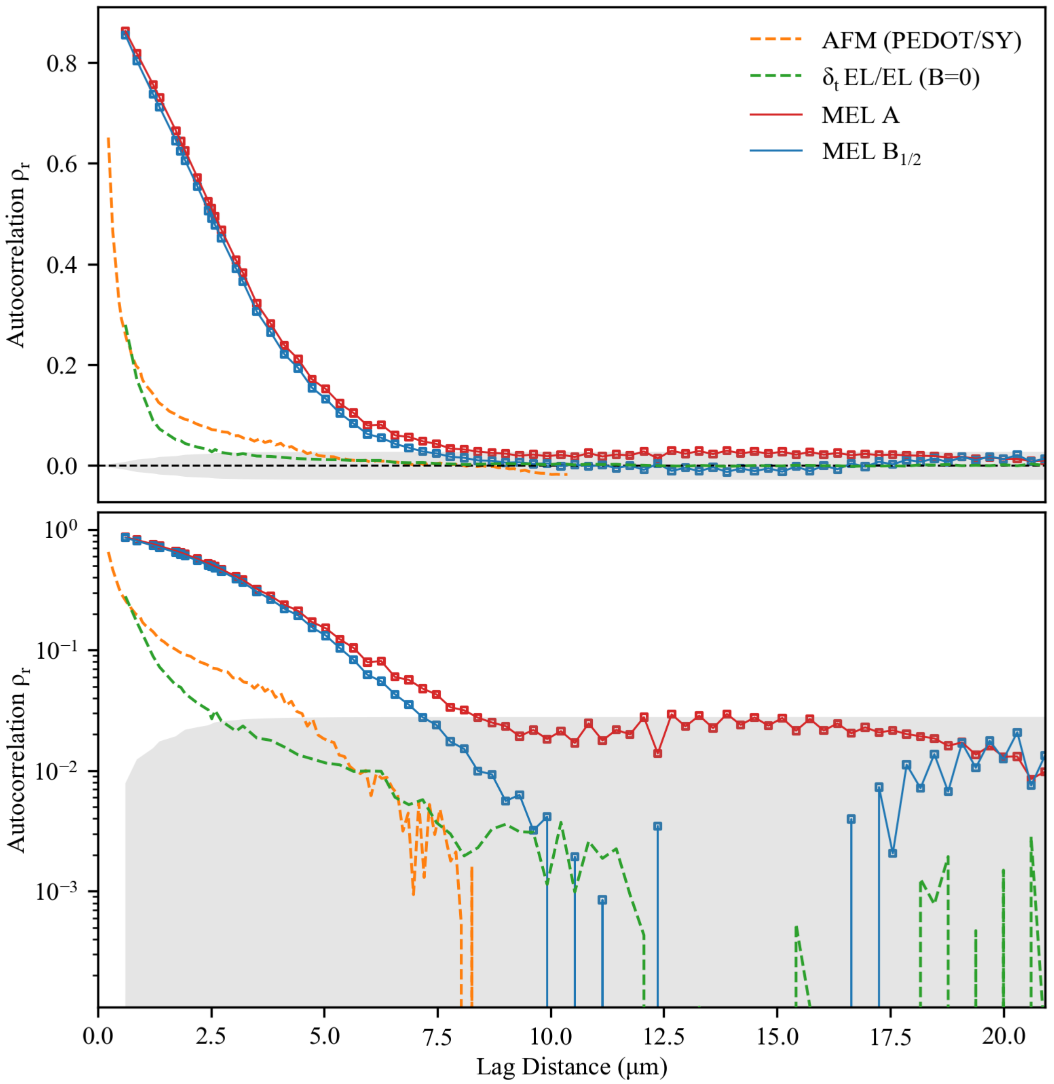


AFM (SY-PPV)

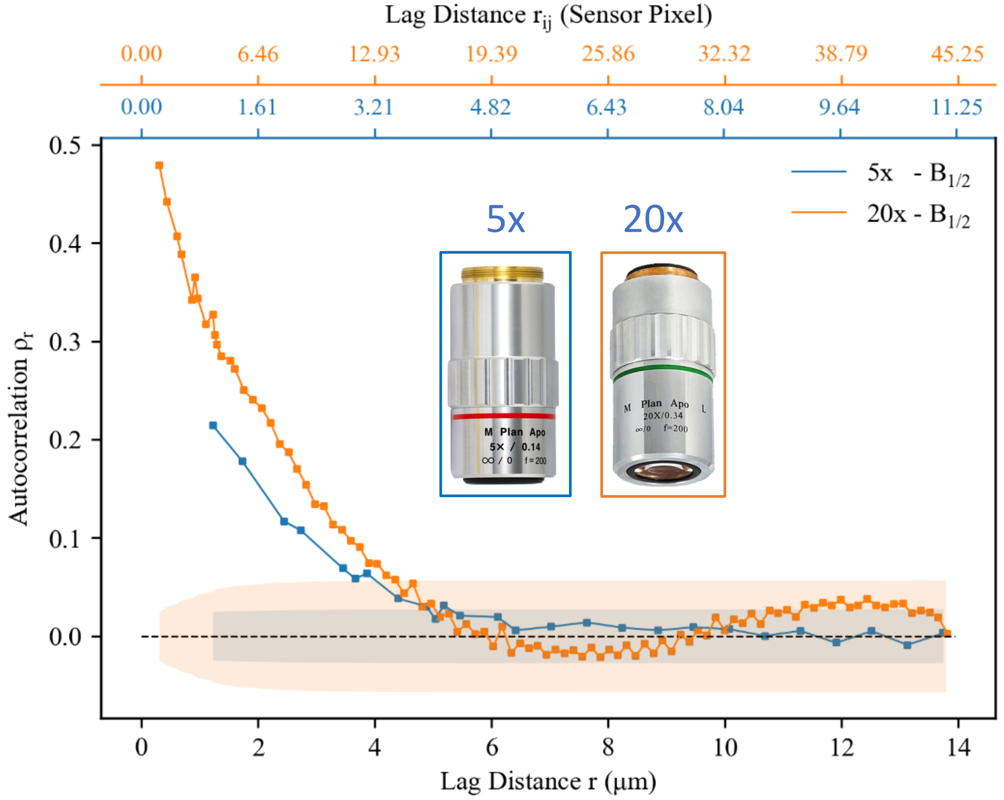


TEM

Separating **spatially-correlated** features

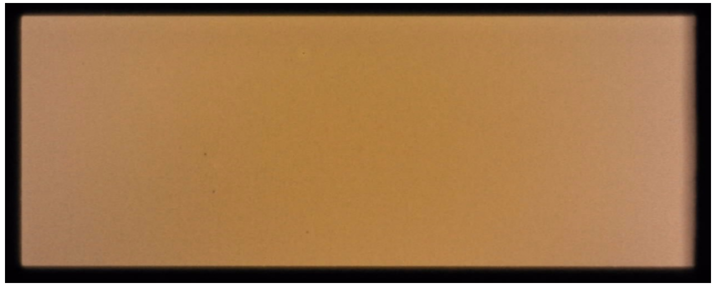


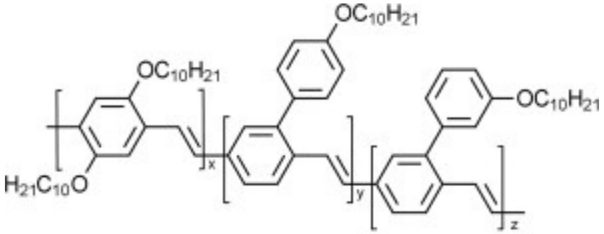
Verifying the **length scales** of correlation

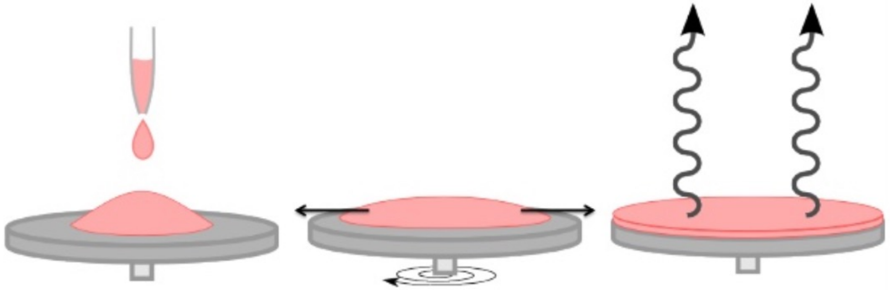


Material Class

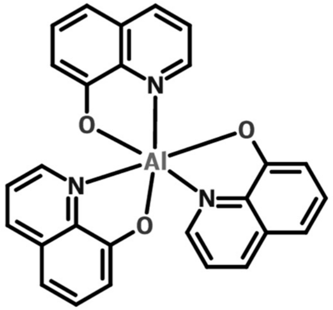
Polymer (SY-PPV)

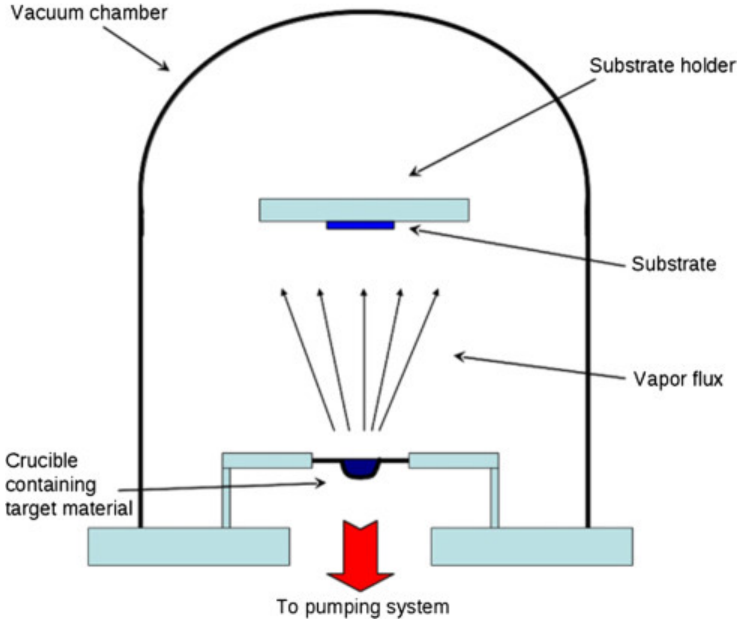






Small Molecule (Alq_3)





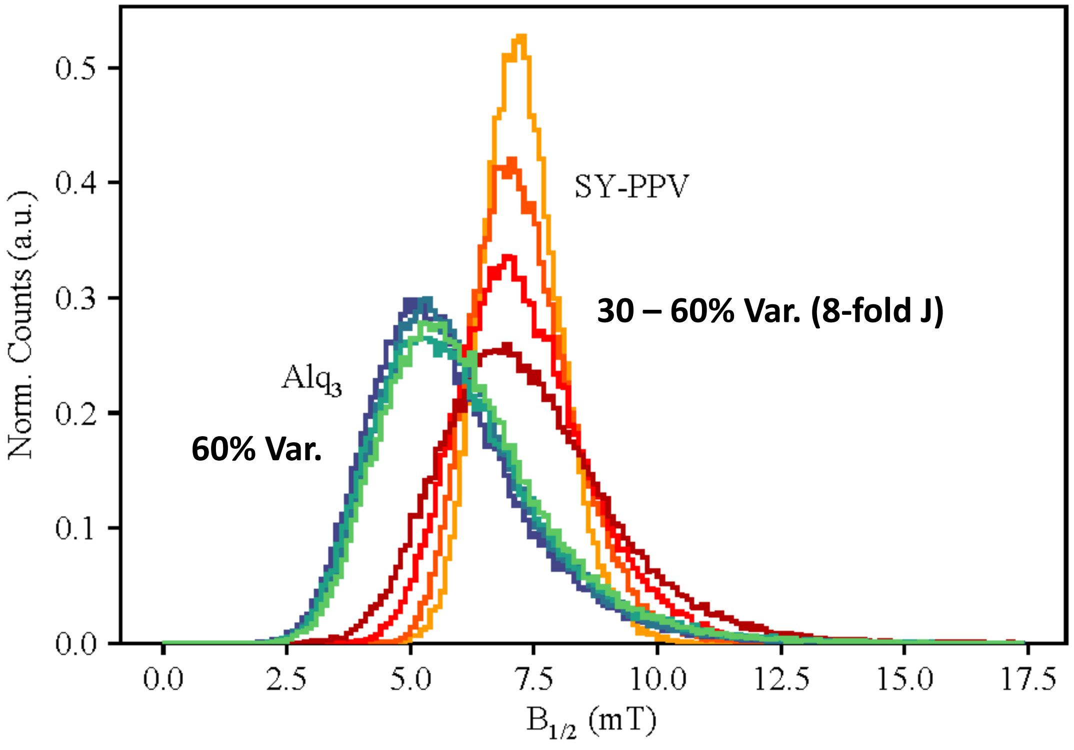
Deposition Technique

Spin Coating

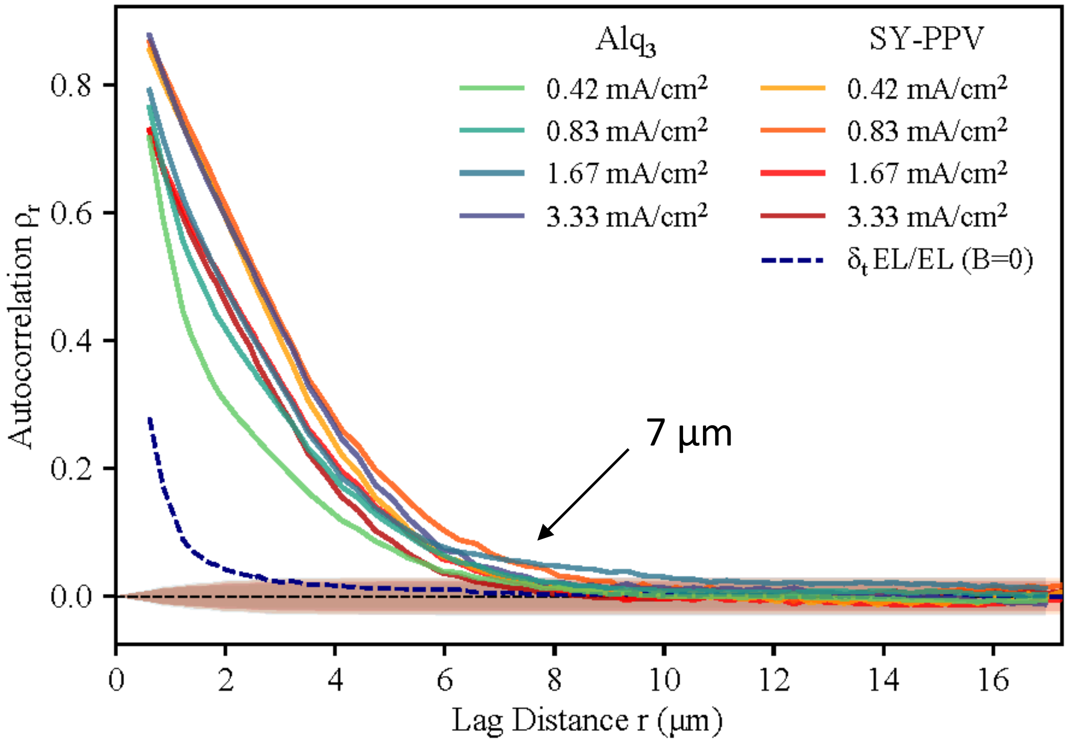
Thermal Evaporation

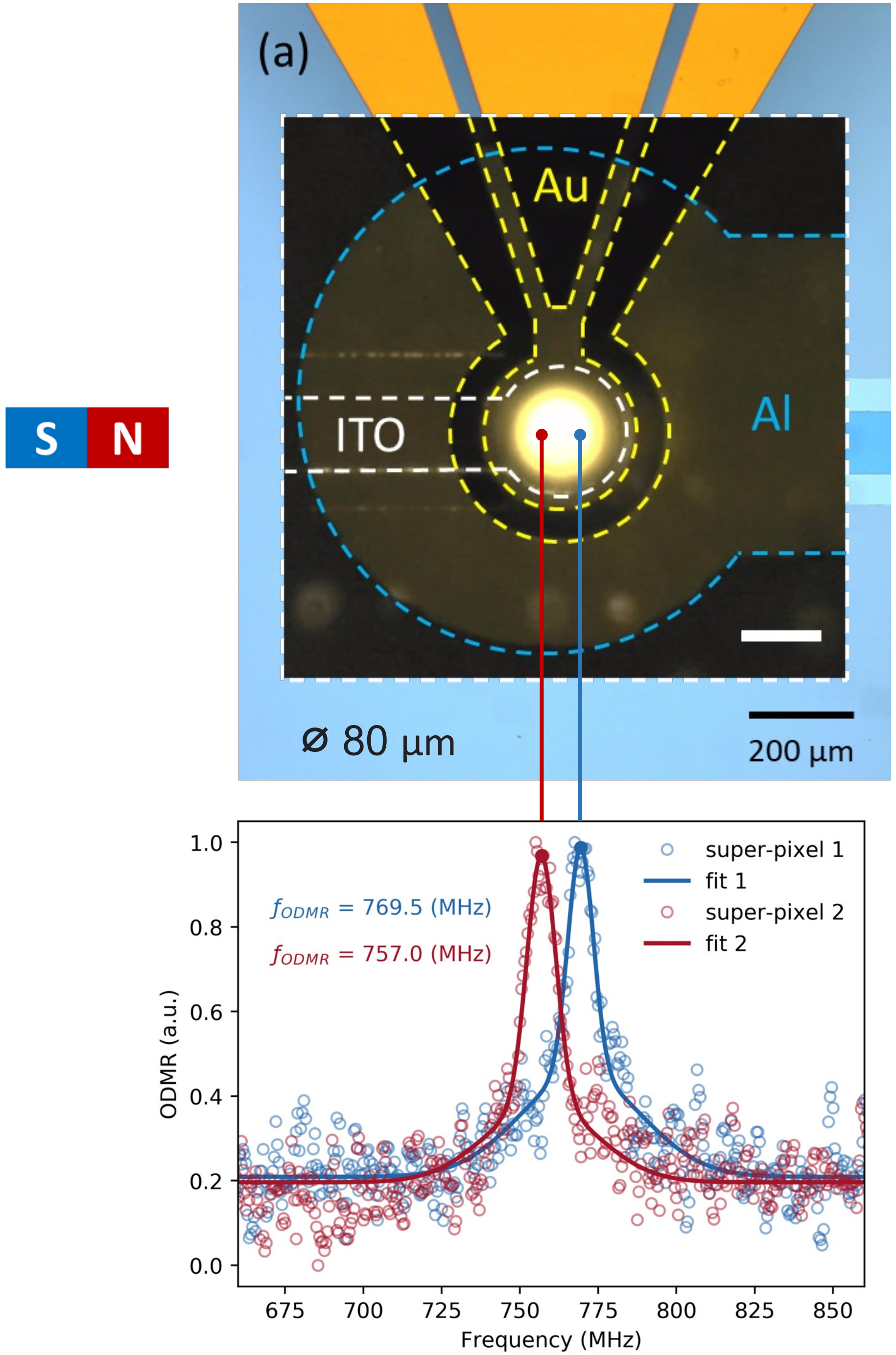
Spin Property Variation: Small Molecule (Alq_3) vs Polymer (SY-PPV)

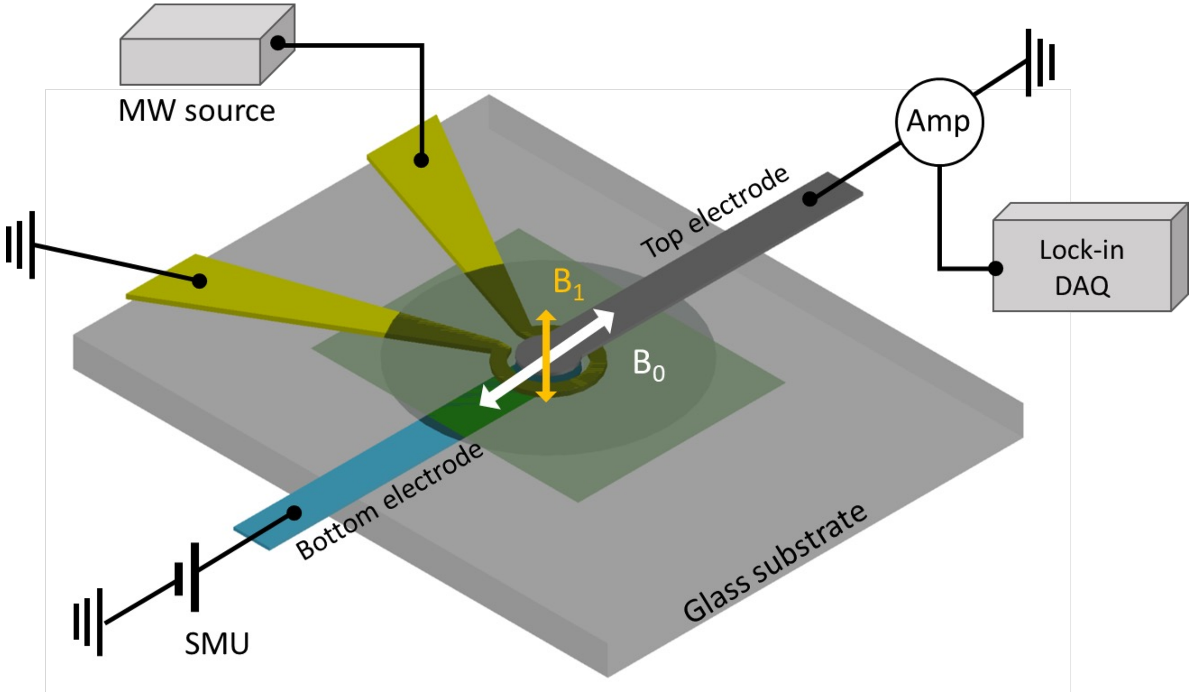
Intra-device Variation ($B_{1/2}$)



Spatial Correlation ($B_{1/2}$)







Integrated 'on-chip' RF resonator for magnetic sensing

Prototype

Sensitivity: ~160 µT $Hz^{-1/2}$ μm^{-2}

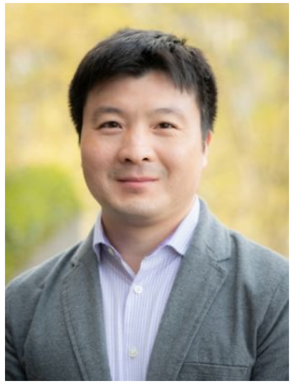
Improvements Underway

Better material magneto-response

Increase CMOS well depth

Improved coupling to B_1 via resonator design

Manuscript Under Review https://arxiv.org/abs/2207.02479



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ELECTRON SPIN RESONANCE

UNSW SYDNEY

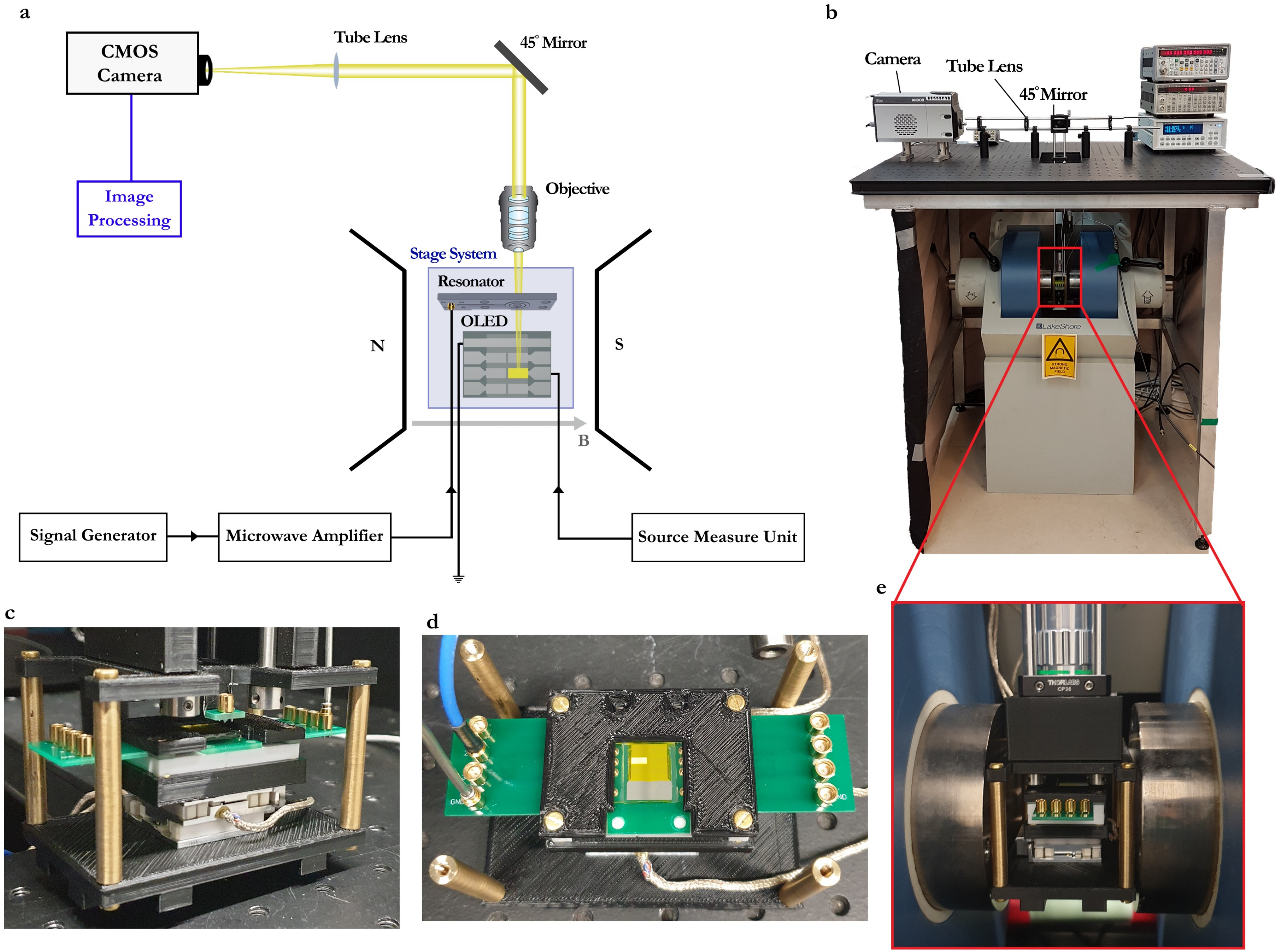
Australian Research Council Centre of Excellence in exciton science

Australian Government Australian Research Council

Supplementary Slides

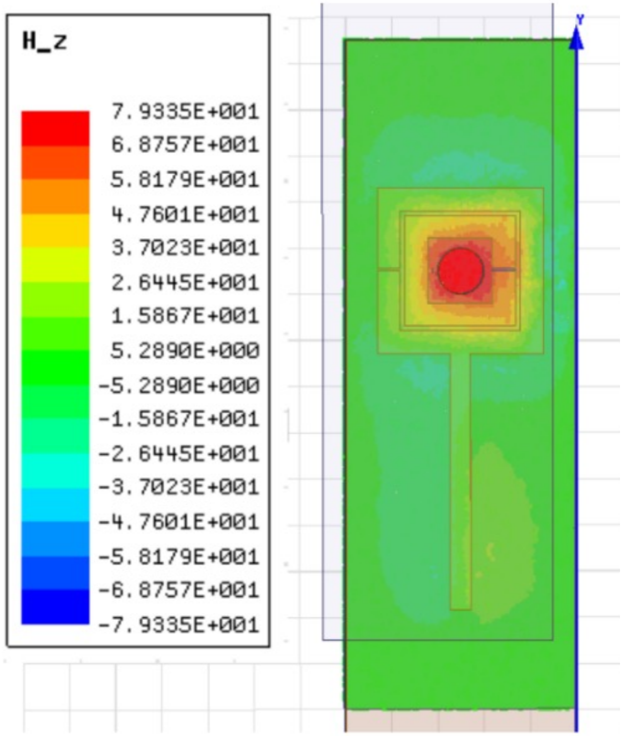
Spatiotemporal Variation

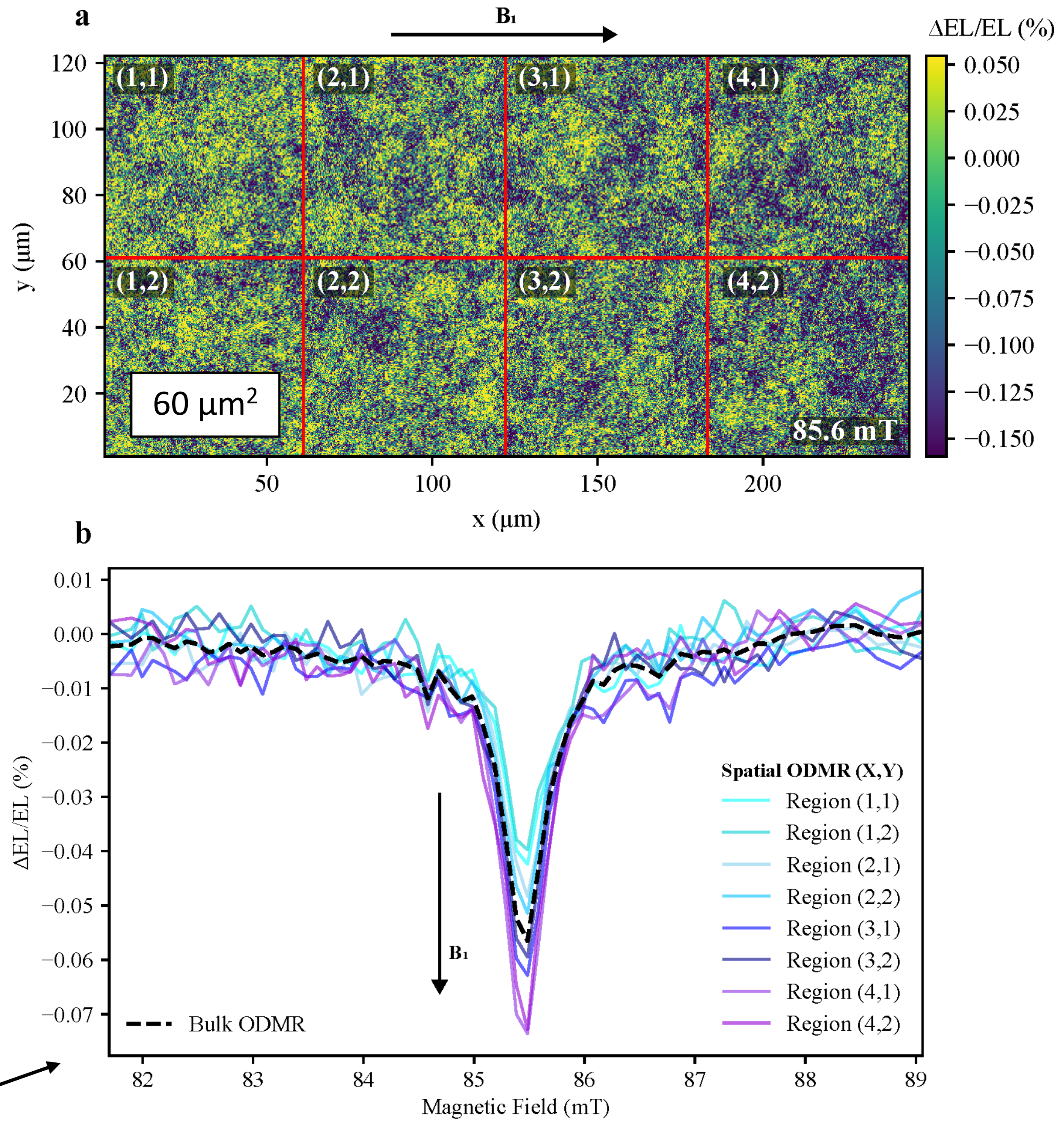
Optically Detected Magnetic Resonance



Spatially Resolved Magnetic Resonance

ODMR amplitude ∝ B_1 magnitude





long time-averaged data

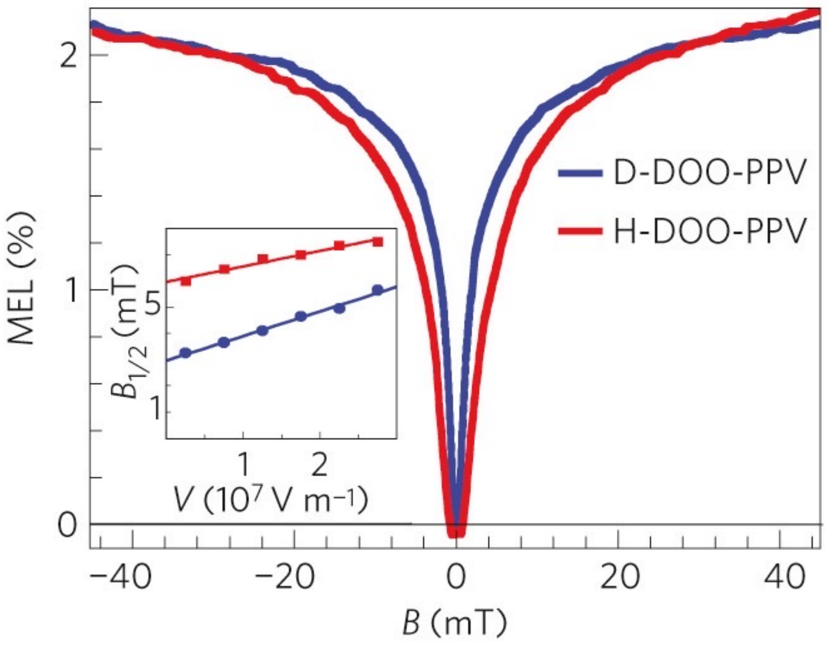
Spin mixing

$\Delta\omega_{hf} + \Delta\theta$

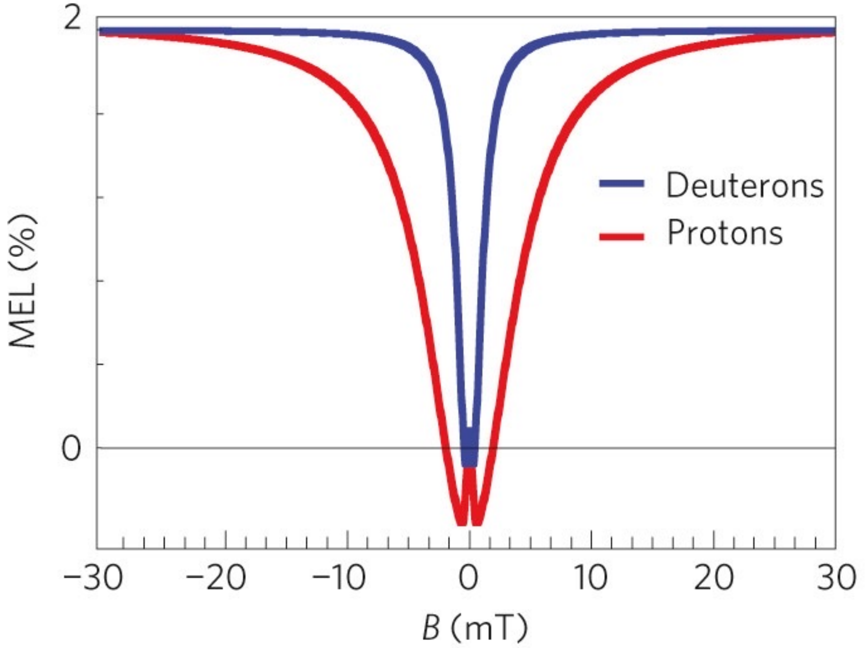
Isotope Exchange

replace all strongly coupled hydrogen atoms (^1H, I=1/2) with deuterium atoms (^2H, I=1)
have much smaller a_{HF}, a(D) = a(H)/6.5

Experiment



Simulation



half-width ($B_{1/2}$) scales with hyperfine interaction strength $\delta B_D \approx 0.5\, \delta B_H$

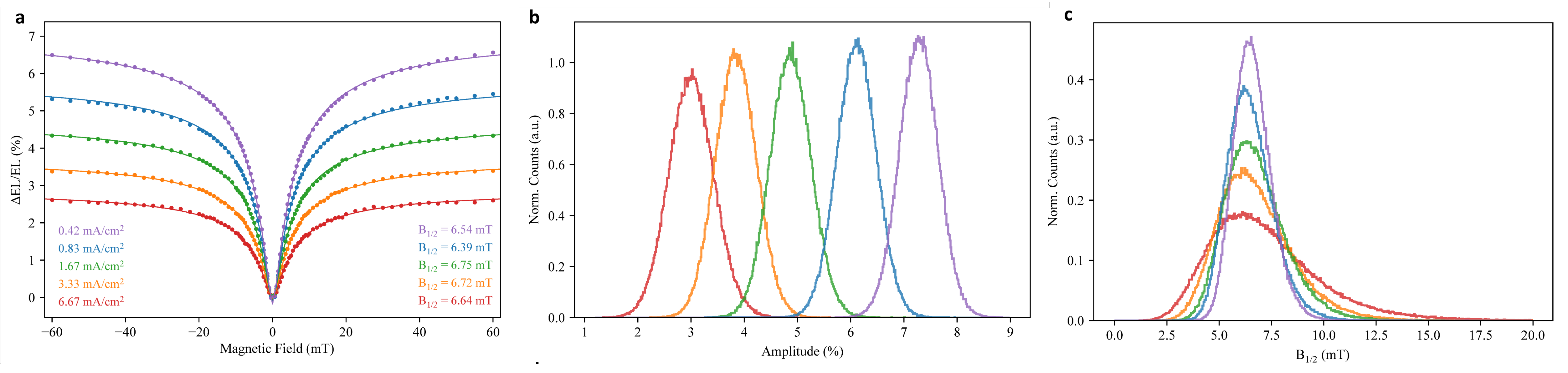
$$\delta B_{hf} = a/\sqrt{N}$$

- Spin density
- Spin dephasing

Polymer (DOO-PPV)	T.D. Nguyen *et al.*, *Nature Mater* **9,** 345–352 (2010)
Small-Molecule (Alq_3)	T.D. Nguyen *et al.*, *Phys. Rev. B, 85* (24), 245437 (2012)

Active Layer Thickness – No Dependence ($B_{1/2}$)

	0.42 mA cm^{-2}	0.83 mA cm^{-2}	1.67 mA cm^{-2}	3.33 mA cm^{-2}	6.67 mA cm^{-2}
SY-PPV (1500 rpm / **110 nm**)	29.2	35.8	49.3*	63.0*	x
SY-PPV (3000 rpm / **70 nm**)	31.1	38.5	48.1*	58.8*	79.6*

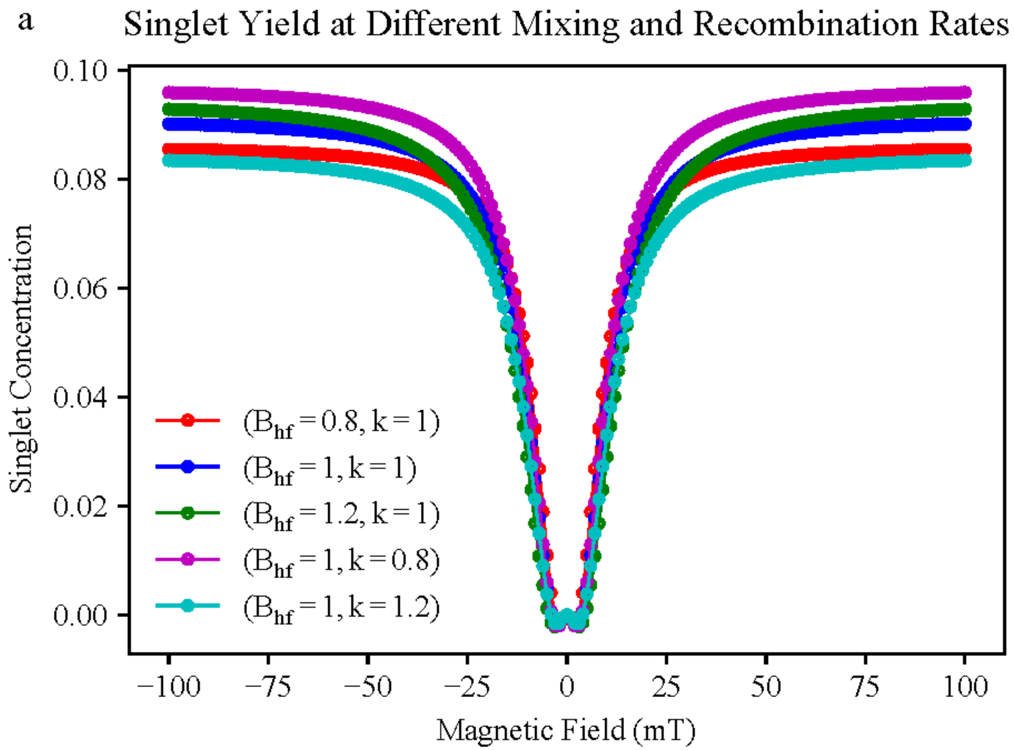


Histogram broadening probably not due to **exciton quenching** processes i.e. **efficiency roll-off**

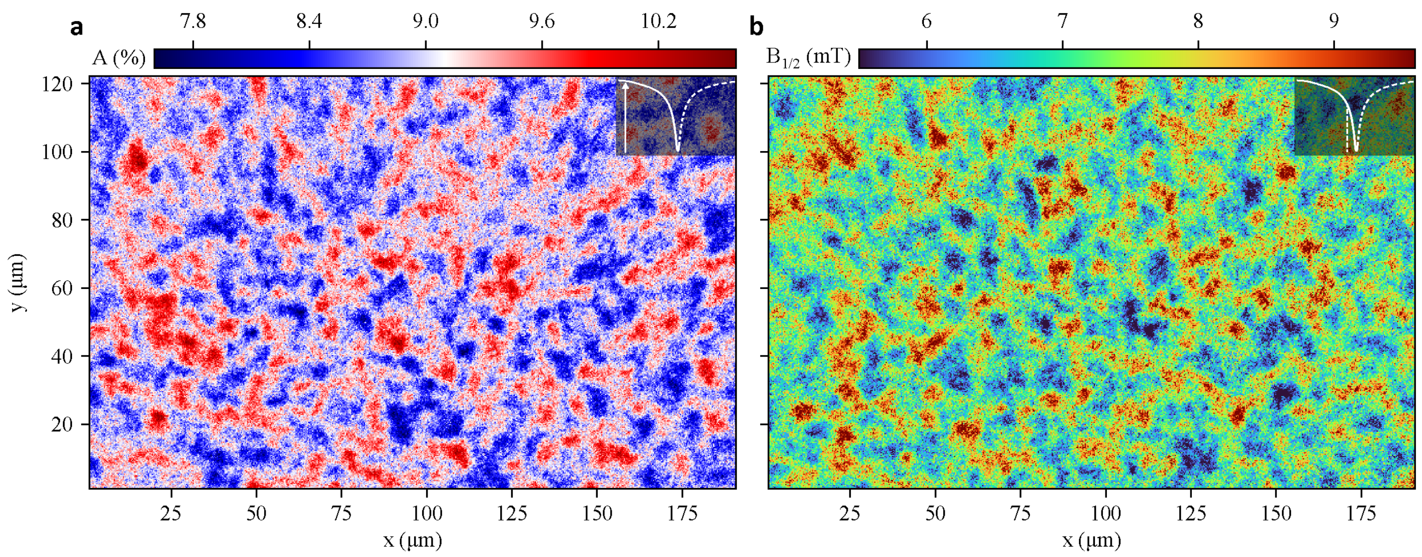
Rate Variation vs. **Hyperfine** Variation

$$\chi_S = \frac{1}{2}\left\{\frac{k_S\frac{1}{2}\sin^2\theta/2}{k_S\frac{1}{2}\sin^2\theta/2 + k_T\left[\frac{1}{2}\sin^2\theta/2+\cos^2\theta/2\right]} + \frac{k_S\frac{1}{2}\cos^2\theta/2}{k_S\frac{1}{2}\cos^2\theta/2 + k_T\left[\frac{1}{2}\cos^2\theta/2+\sin^2\theta/2\right]}\right\}$$

Kersten *et al.*, *Phys. Rev. Lett.* **106**, 197402 (2011)

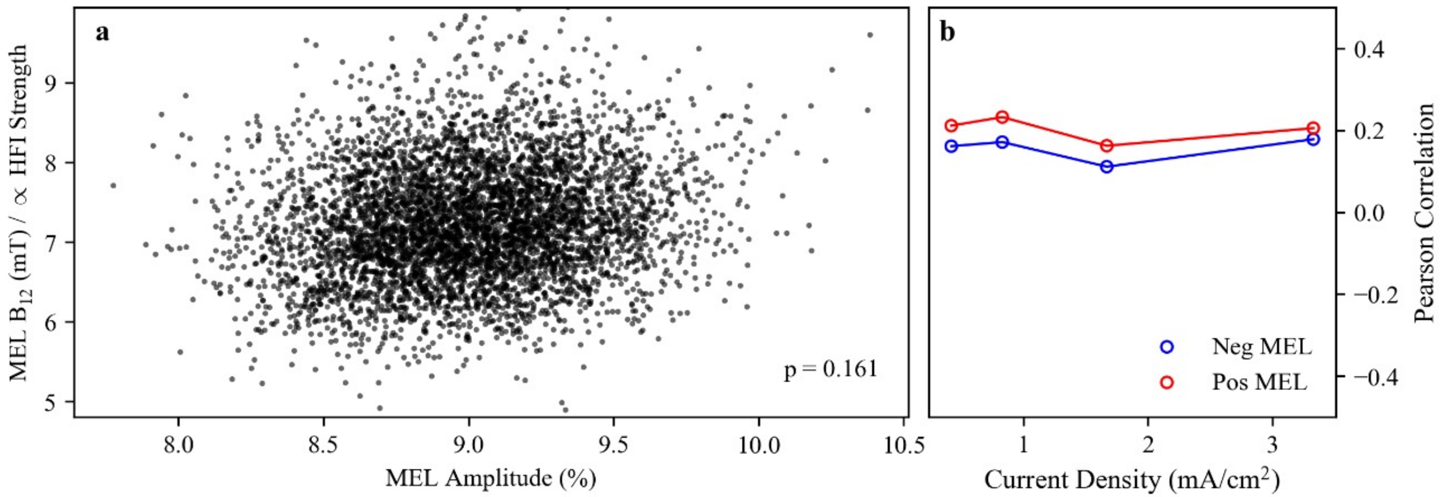


Rate Variation vs. **Hyperfine** Variation

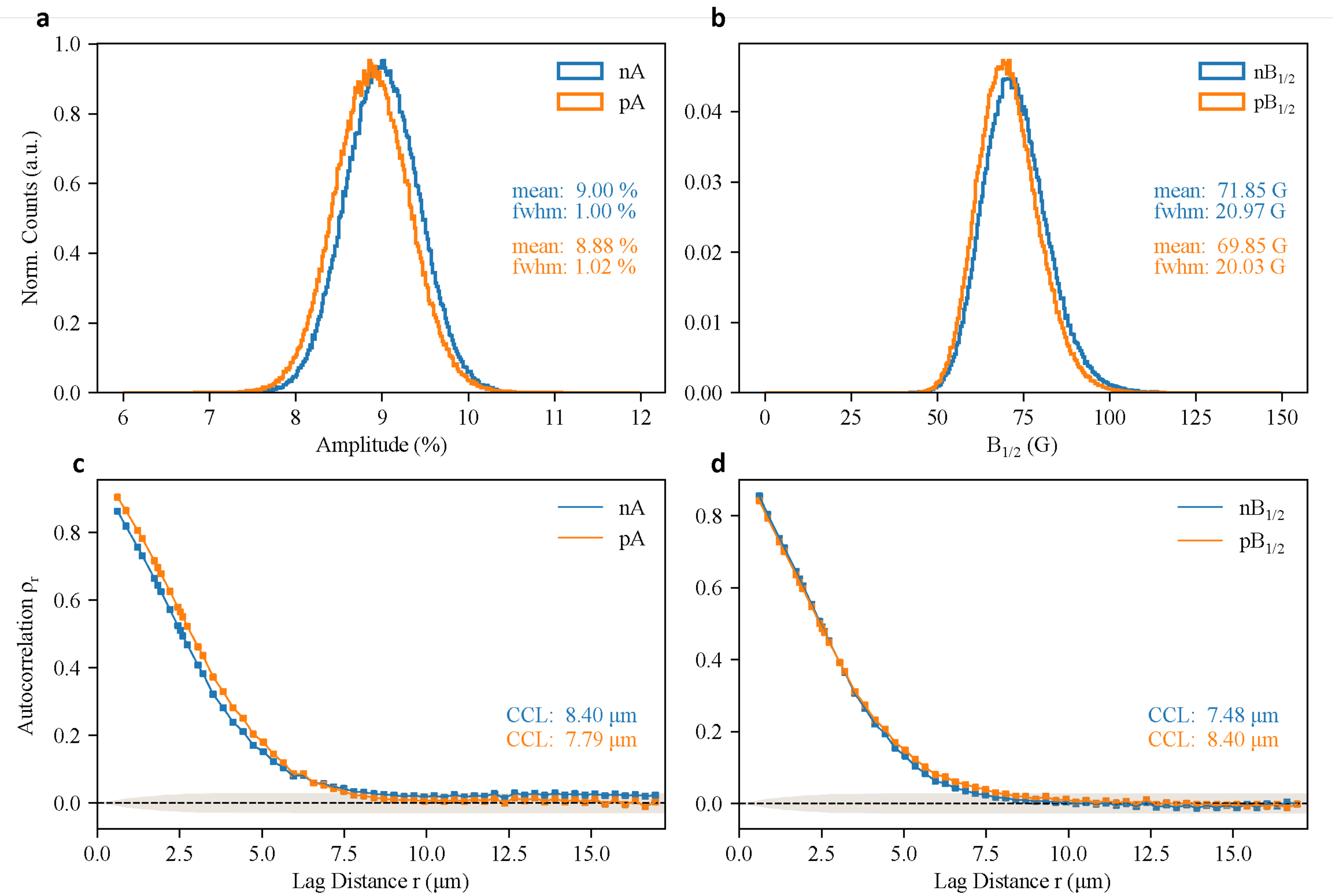


250k points

Correlation coefficients remain **positive** and **significant** (~0.2 with a 2-sided p-test < 10^{-5})



Global Spatiotemporal Evolution: **Neg / Pos Polarity** Field Sweeps



Ruled Out

Spatial Correlation of MEL not adequately explained by:

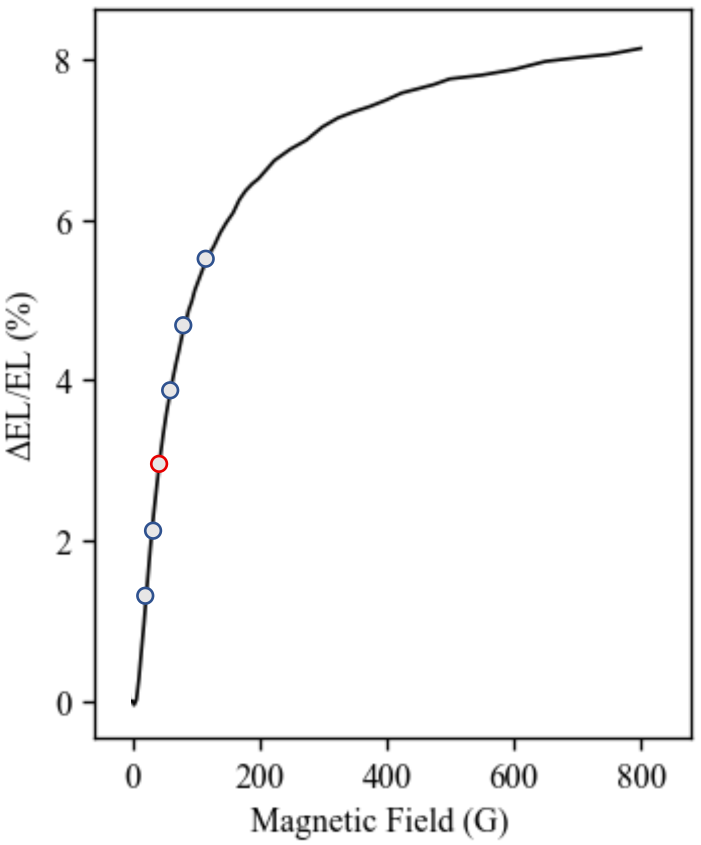
- Aggregates / Film Homogeneity (AFM, TEM, MEL dynamics)
- Molecular Material (polymer vs small-molecule)
- Exciton Quenching Processes (active layer thickness)
- Spatial Coherence of OLED (time-correlated EL maps)
- Recombination Rate Variation (positive Pearson A vs $B_{1/2}$)

Contributing factors:

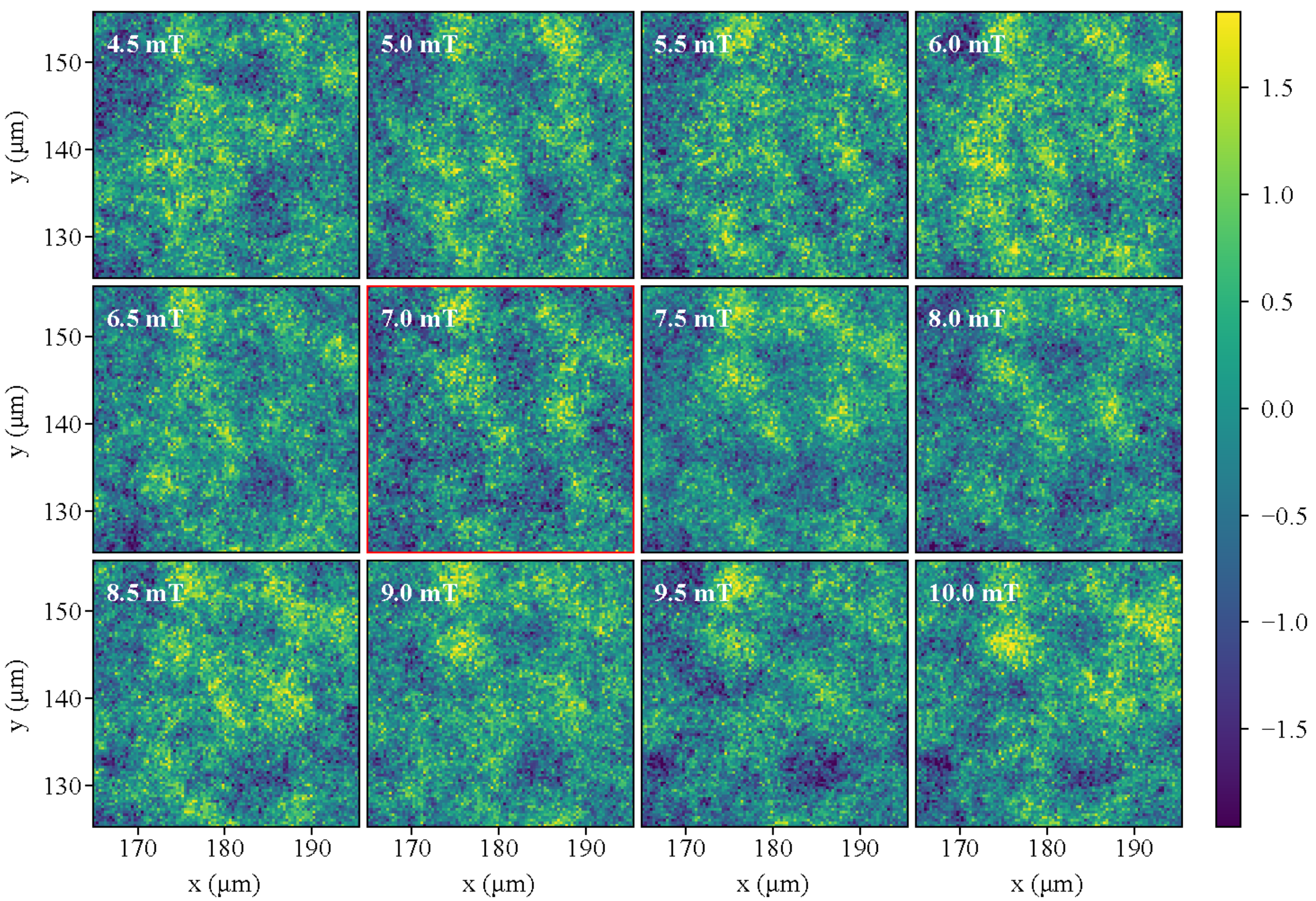
- Hyperfine Variation + Diffusion (MEL $B_{1/2}$, A-$B_{1/2}$ correlation, dynamics)
- Exchange Variation (Spin-mixing variation, range of $r_{e\text{-}h}$)
- Hopping Rate Variation (MEL lineshape dependence)
- Interface Effect (Bulk vs. Active-LiF/Al effect)

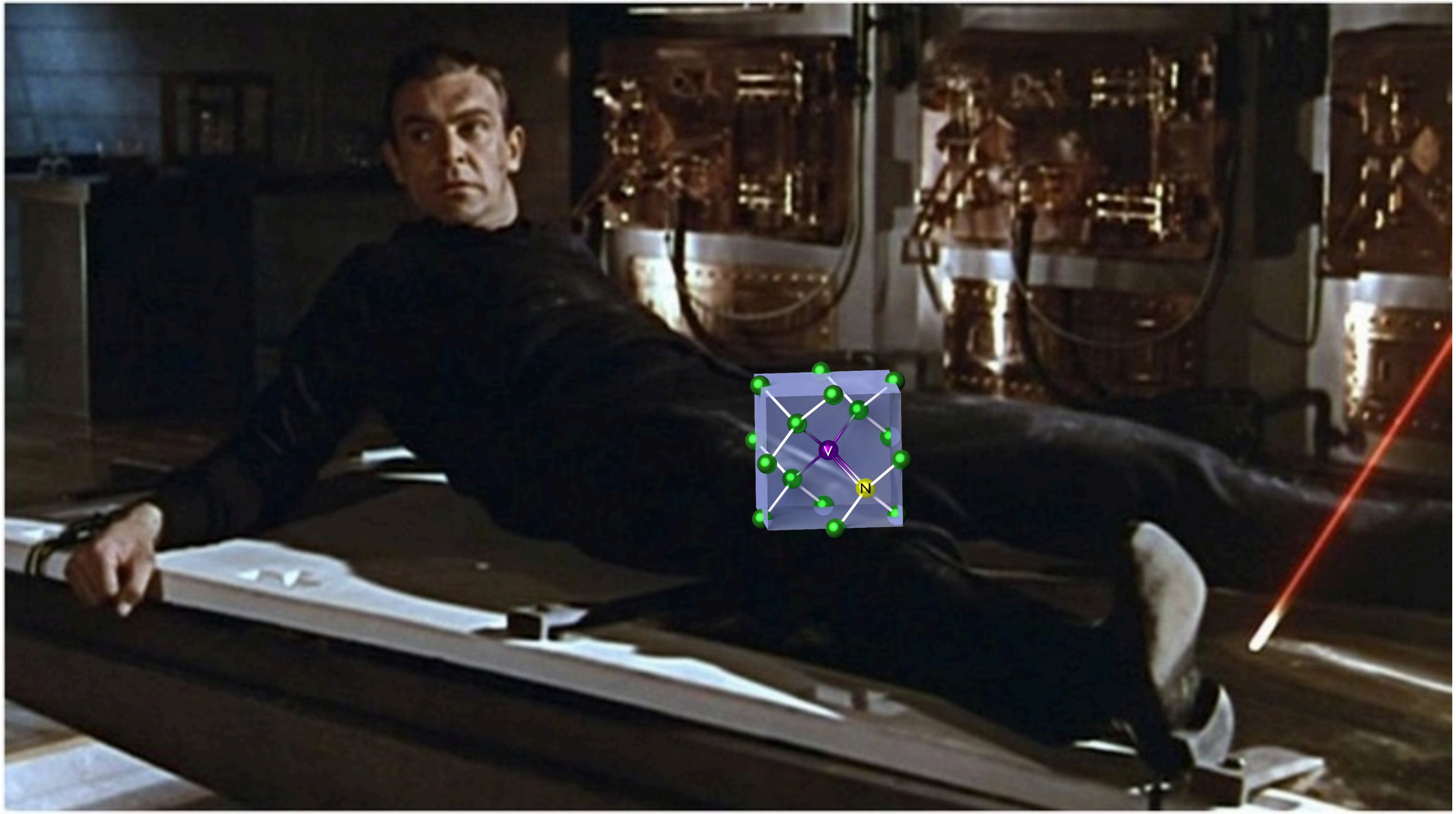
Possible Sources

Integrated EL



Spatio**temporal** Evolution




V
N