Spin Exchange Between Triplet ^{3}CS and ^{3}LE states in NI-PXZ dyad revealed by TR EPR

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ITC SB RAS
VVV-2022

Outline

- Introduction
- TR EPR theory and experimental
- TR EPR results
- Results of other techniques
- Conclusion

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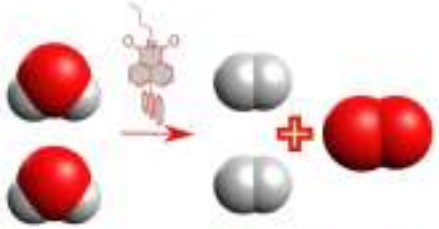
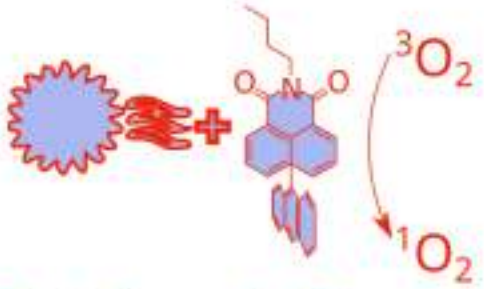
Introduction

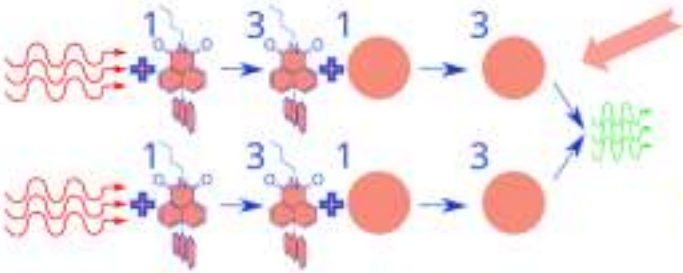
Photoredox Catalysis



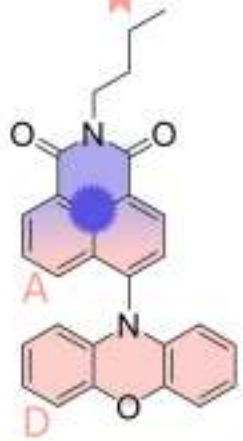
Hydrogen Production



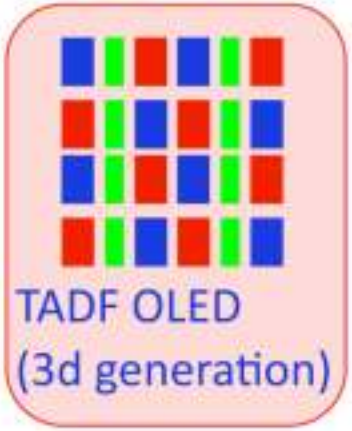
Photodynamic Therapy



Triplet-triplet annihilation upconversion



D-A compounds



TADF OLED (3d generation)

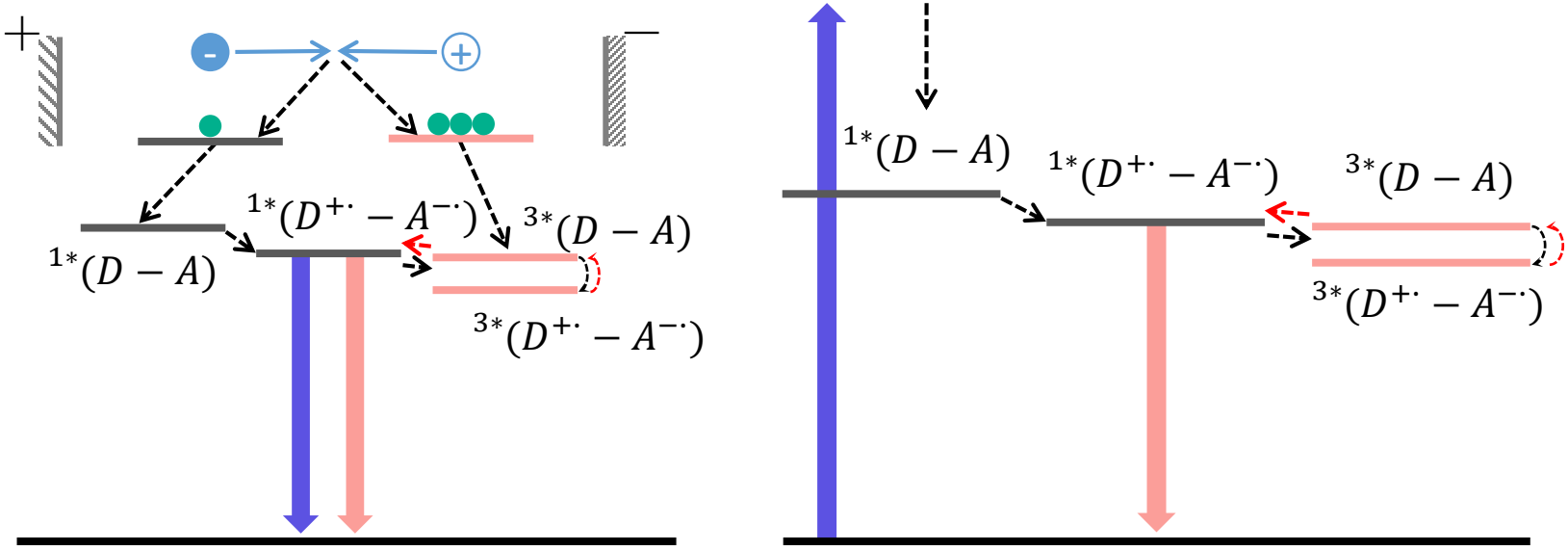
$$U_{CNOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

Quantum Information Science

TADF OLED

TADF = Thermally Activated Delayed Fluorescence

OLED = Organic Light Emitting Dyode



- TADF OLEDs are the next generation of OLEDs with ~100% internal quantum efficiency
- The crucial step is ^{3}CT-^{3}LE exchange (vibronic coupling)
- TR EPR spectroscopy elucidates this process

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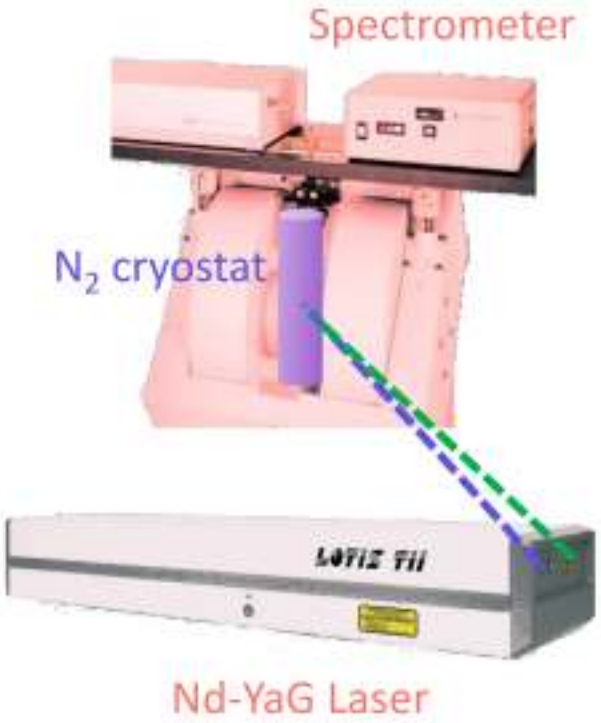
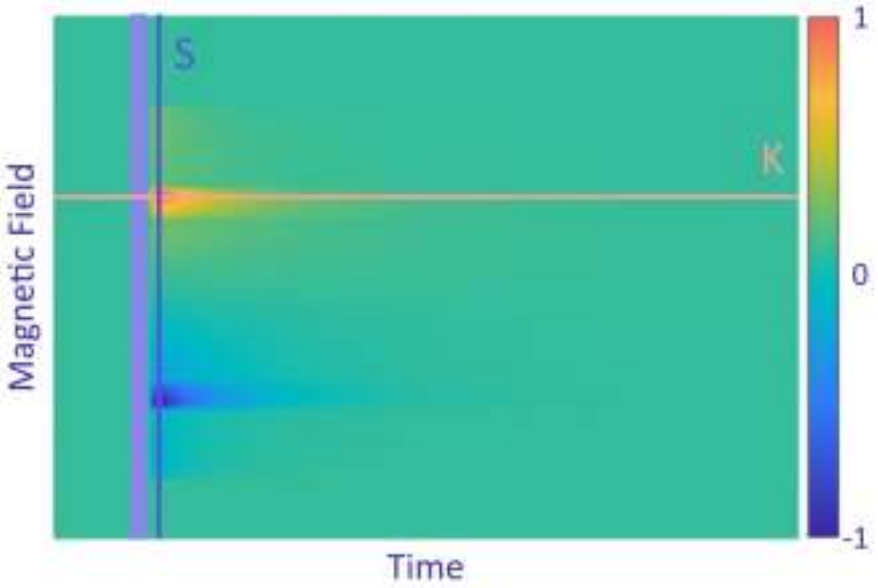
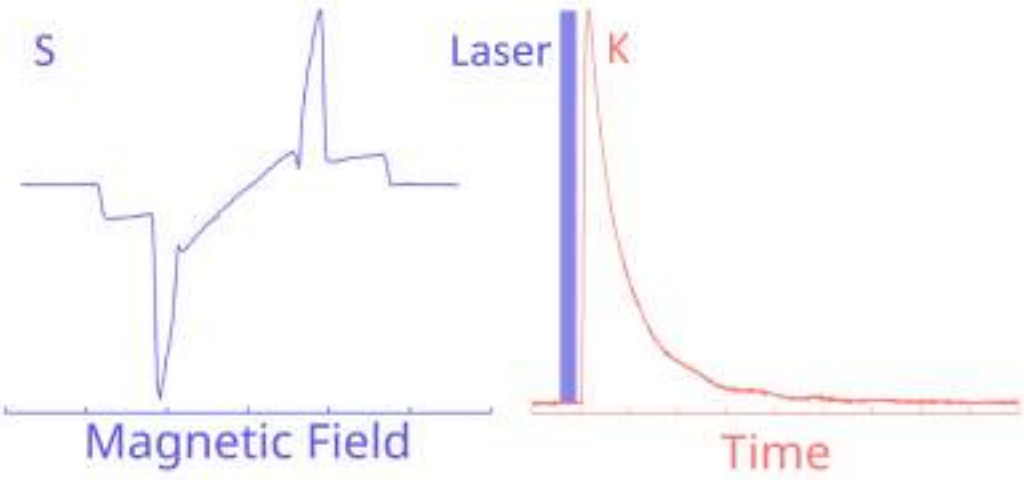
TR EPR. Experiment





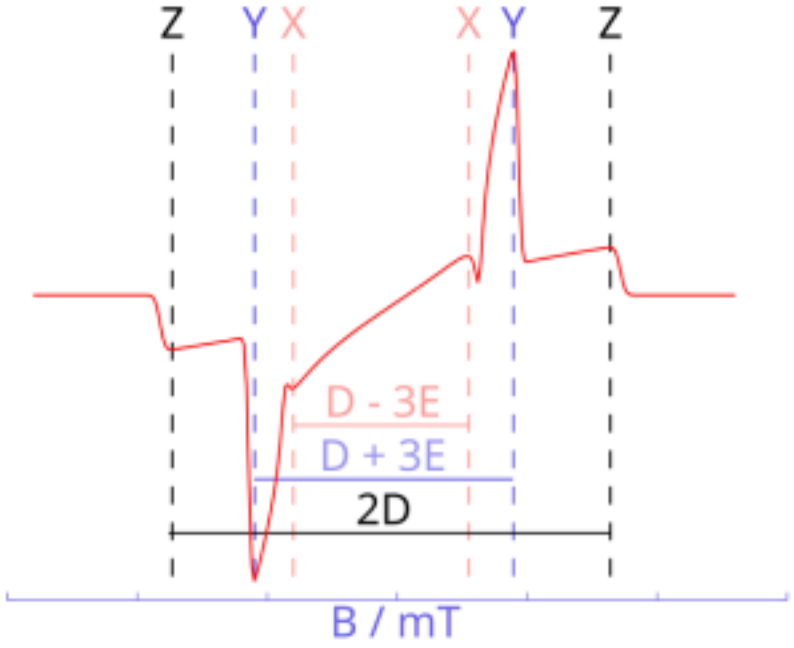


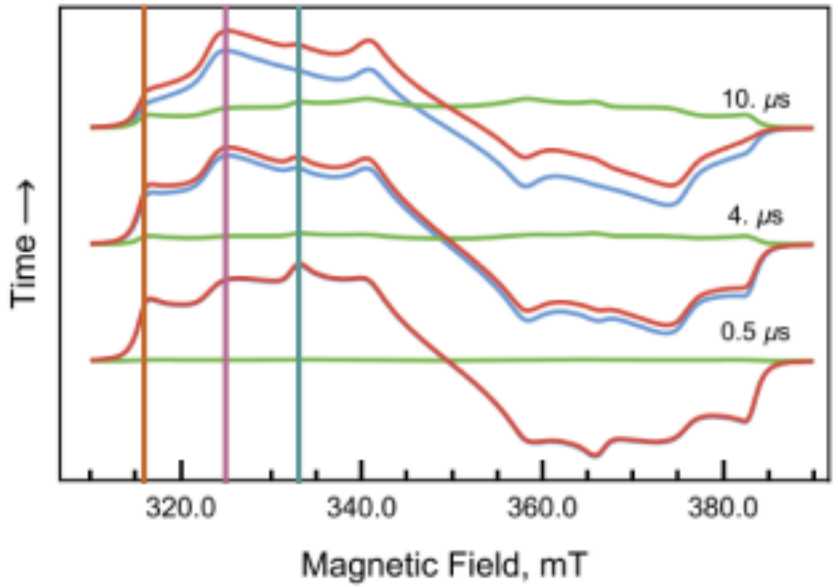
Time Resolved EPR. Theory

$$\hat{H}_{EPR} = g\beta\vec{B}\hat{g}\hat{\vec{S}} + \hat{\vec{S}}\hat{D}\hat{\vec{S}};$$

$$\hat{D} = g_1 g_2 \beta^2 \langle \frac{1}{r^3}(\delta_{ij} - 3n_i n_j)\rangle$$

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





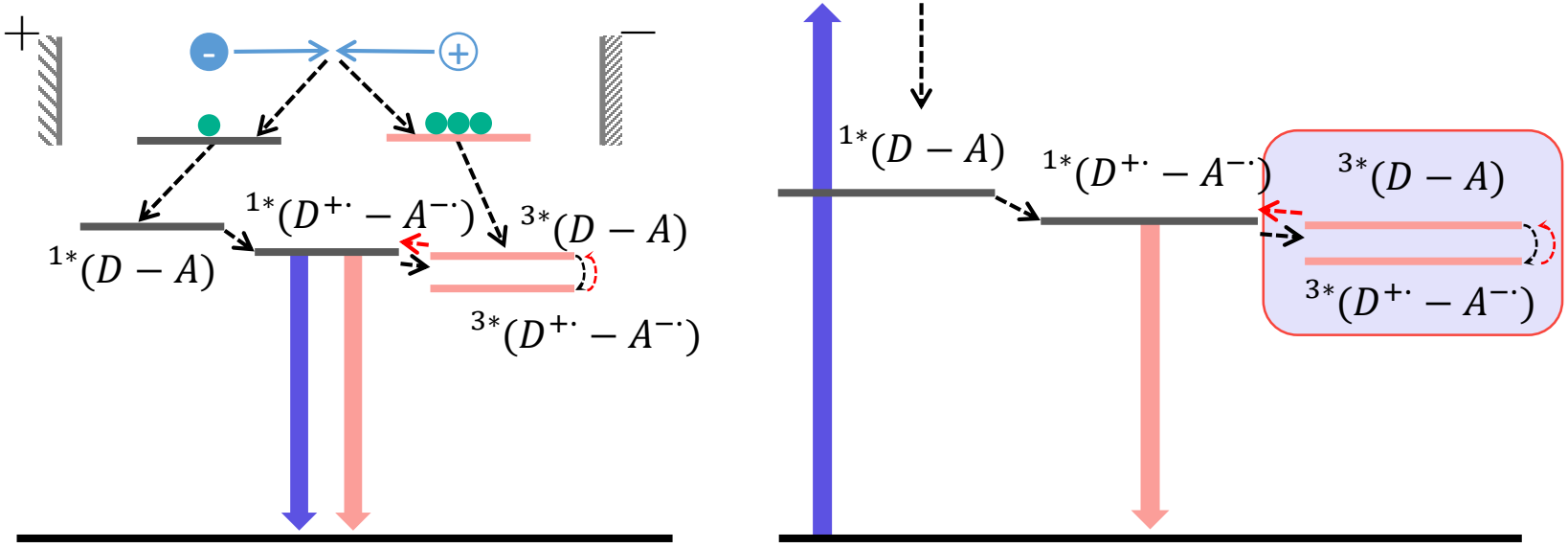
J. Chem. Phys. 153, 094304 (2020); doi: 10.1063/5.0022164

- TR EPR reveals:
  - The spin density localization
  - The spin dynamics of triplet states

TADF OLED

TADF = Thermally Activated Delayed Fluorescence

OLED = Organic Light Emitting Dyode



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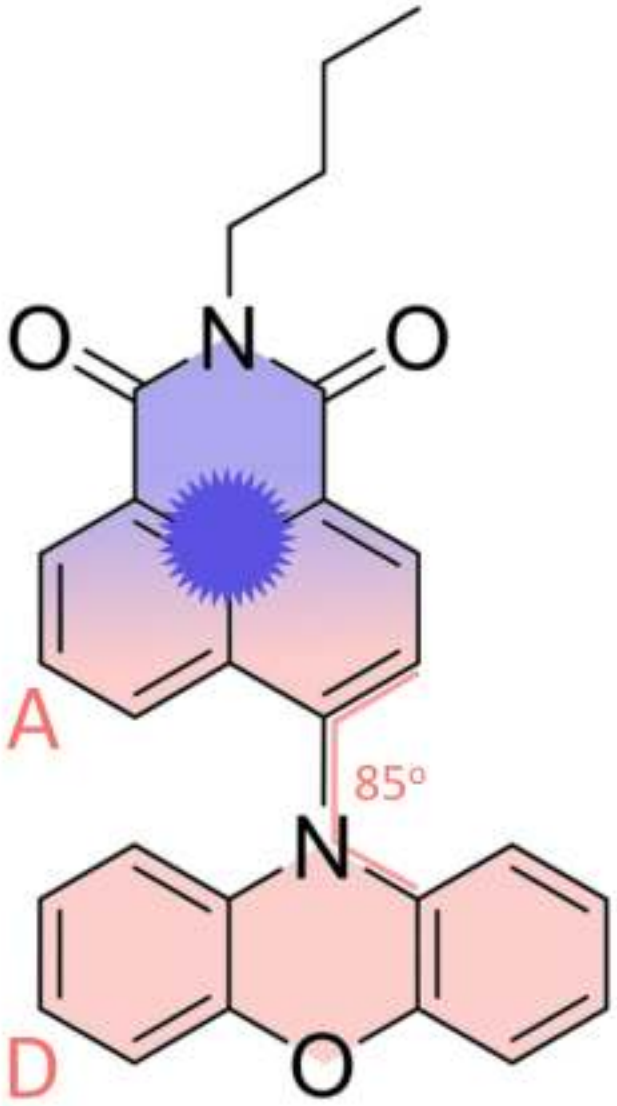
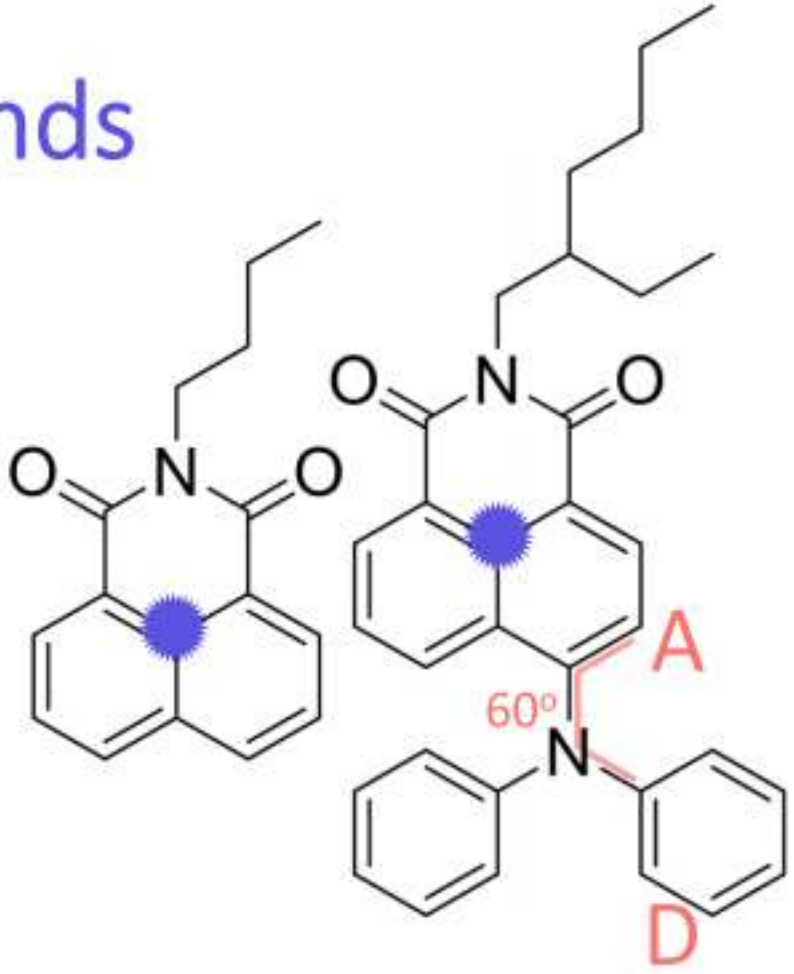
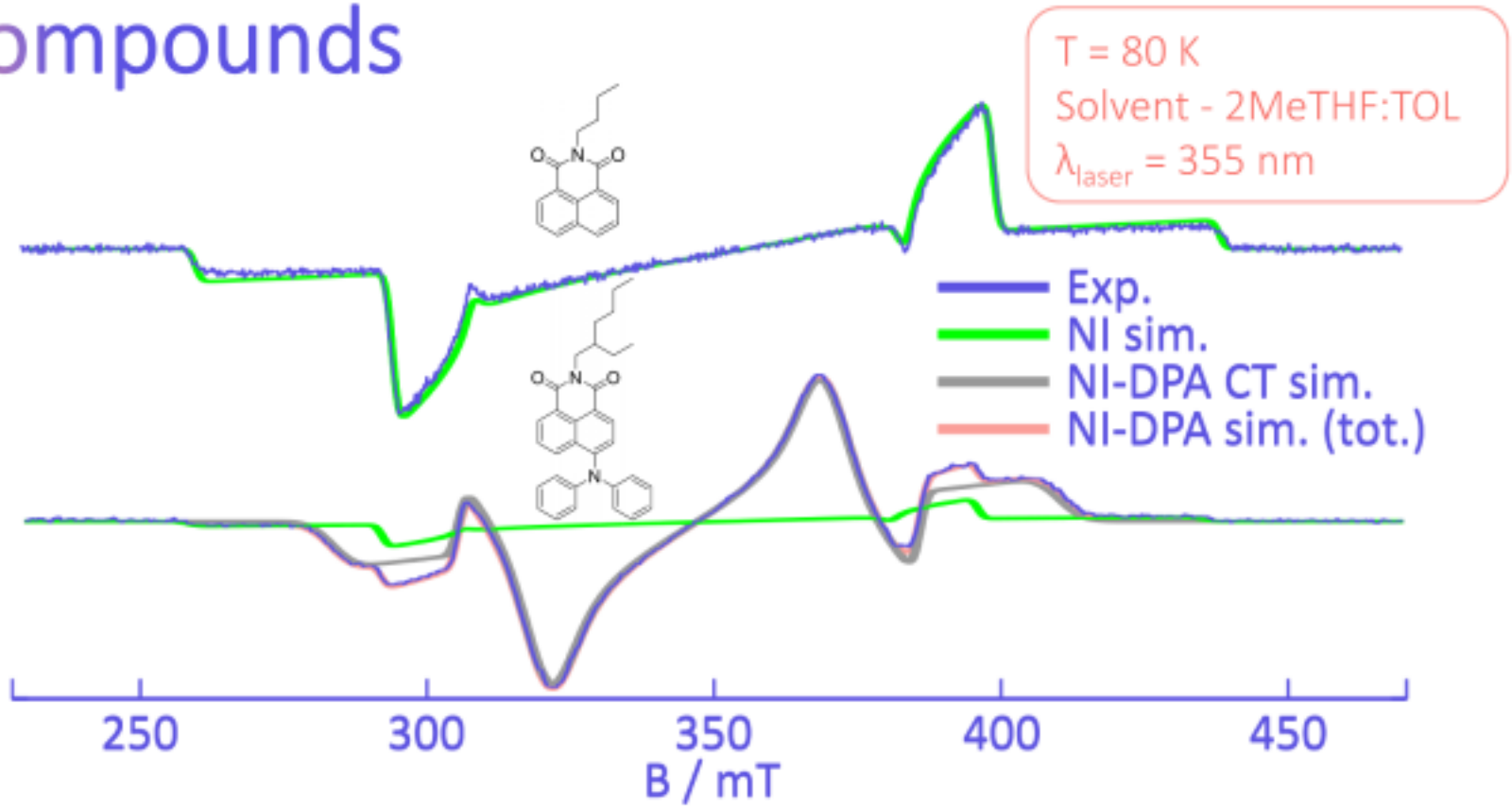
Studied Compounds





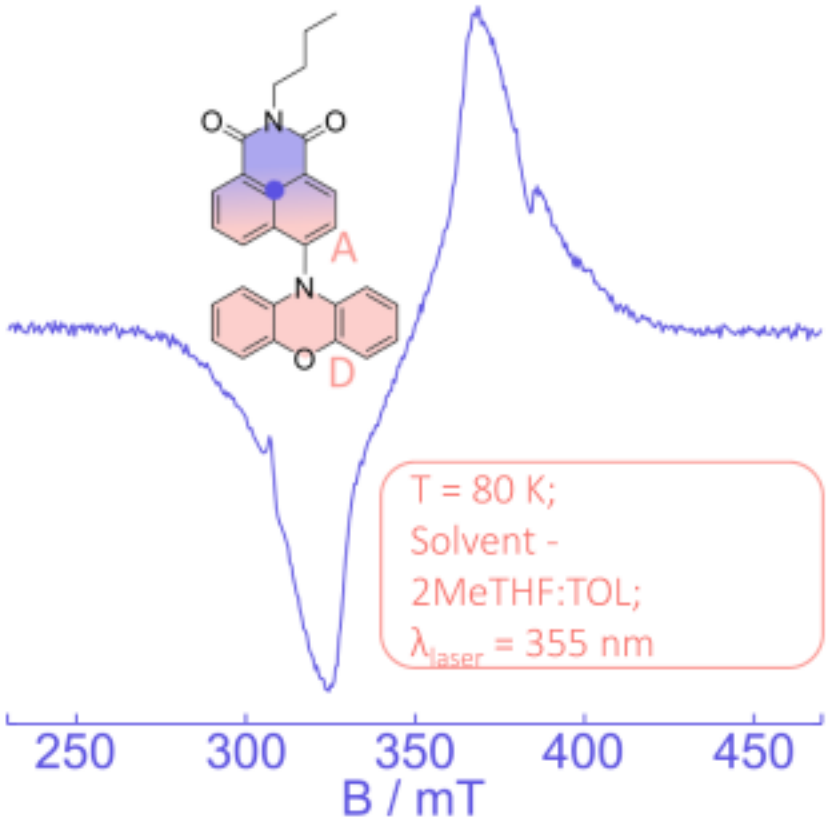
- T = 80 K
- Solvent - 2MeTHF:TOL (1:3)
- λ_{laser} = 355 nm

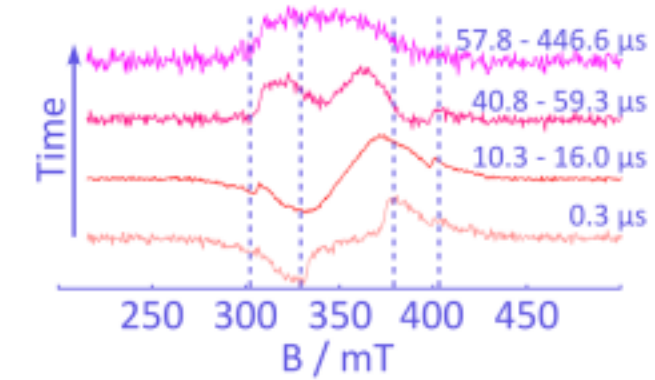
TR EPR spectra. Reference Compounds

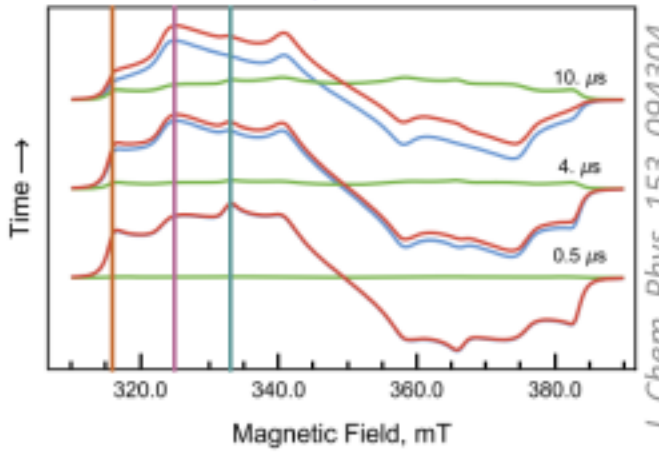


- NI features a simple triplet spectrum
- NI-DPA spectrum is comprised of ^{3}NI-signal and a signal of a more delocalized triplet (^{3}CT - ?)

TR EPR spectra. Lineshape and Evolution







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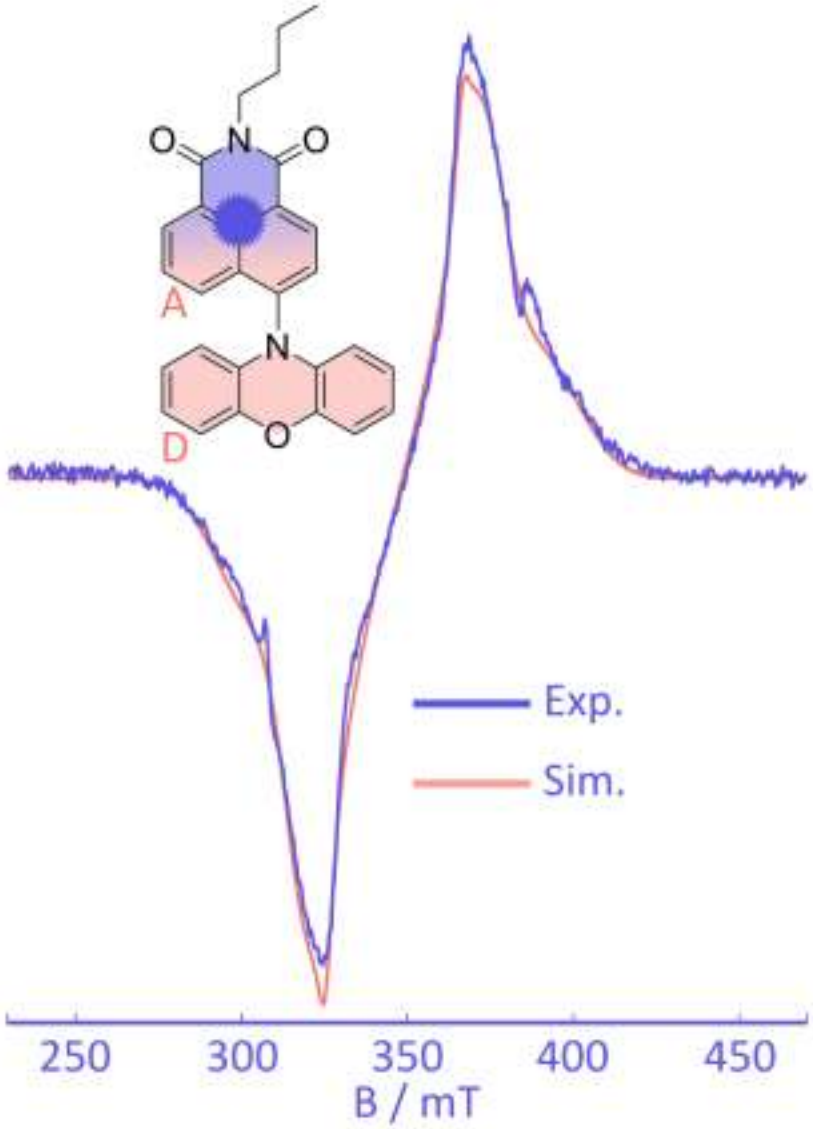
- The lineshape of NI-PXZ spectrum indicates an triplet exchange
- The evolution of the spectrum supports the exchange hypothesis

TR EPR spectra. Simulation and Model



$$\widehat{D}_{eff} = \frac{\widehat{D}_1 + \widehat{D}_2}{2}$$

	D, MHz	E, MHz
^{3}NI-PXZ $_{(eff)}$	1484	109
^{3}NI	2475	135
^{3}CT	493	83

- The effective parameters of the spectrum simulation suggest ^{3}NI-^{3}CT exchange

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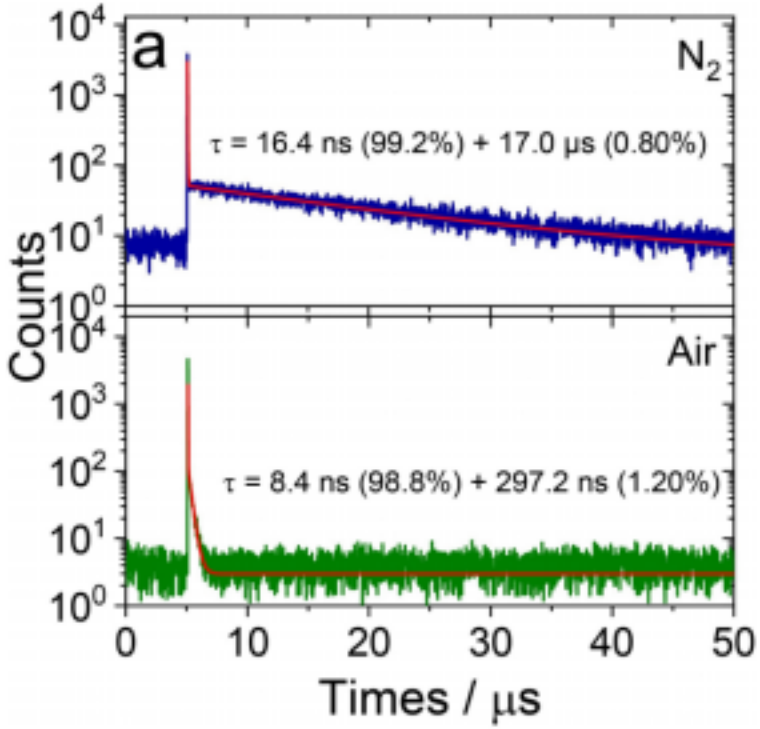
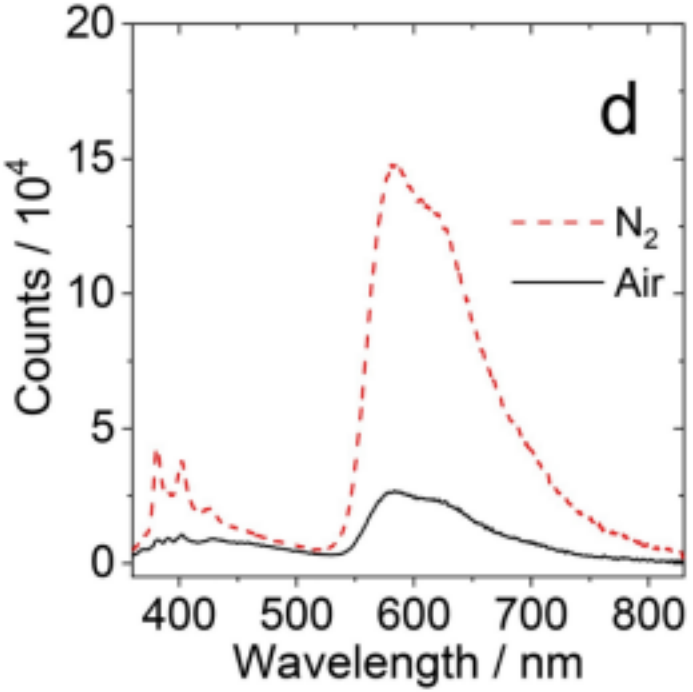
Support from Optics



NI-PXZ fluorescence decay; λ_{ex} = 340 nm; λ_{tr} = 580 nm; T = 25°C

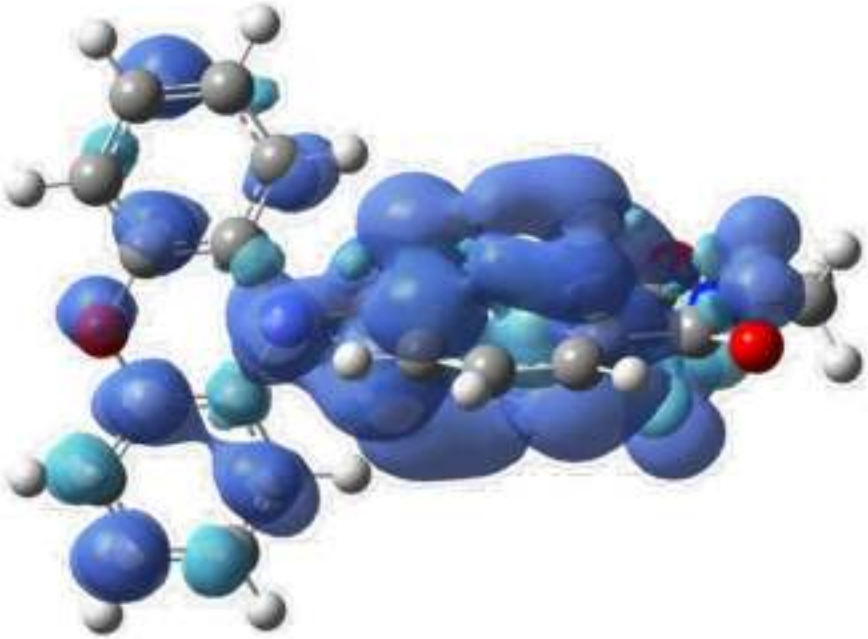


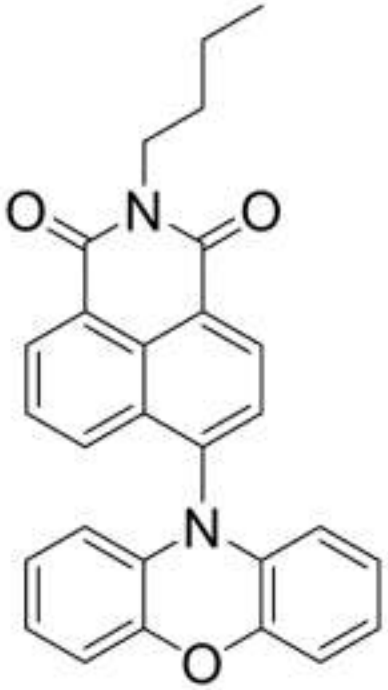
NI-PXZ fluorescence spectrum; λ_{ex} = 340 nm; T = 25°C

- Fluorescence data indicates the presence of ^{1}CT with TADF character

Chem. Eur. J. 2022, 28, e202200510; doi: 10.1002/chem.202200510

Support from DFT





Spin density surfaces of ^{3}NI-PXZ in vacuum. CAM-B3LYP/6-31G(d) with Gaussian 09 (isoval=0.0010)

- DFT shows the lowest triplet state with a strong CS character

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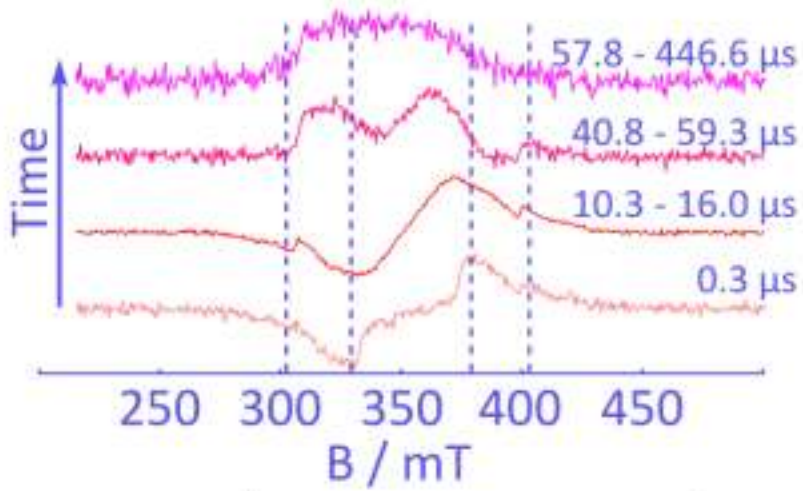
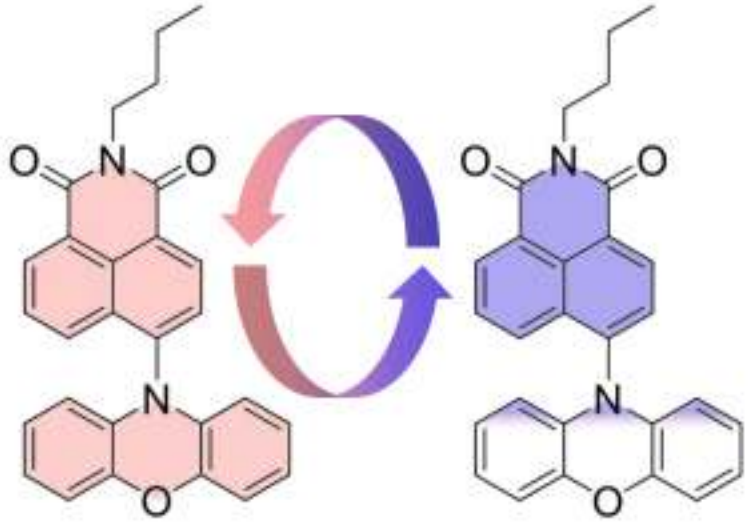
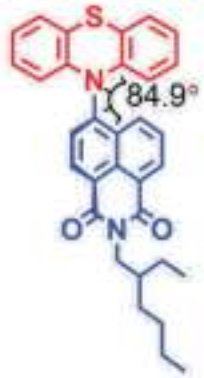
Concluding Remarks



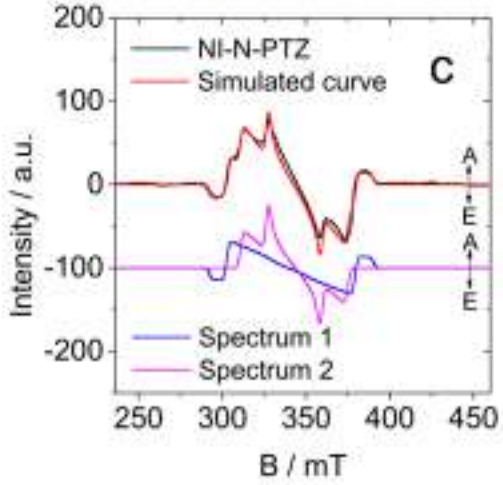


- ✓ TR EPR reveals ^{3}LE-^{3}CT exchange in a TADF dyad NI-PXZ
- ✓ TR EPR is an important tool for the TADF OLED materials study

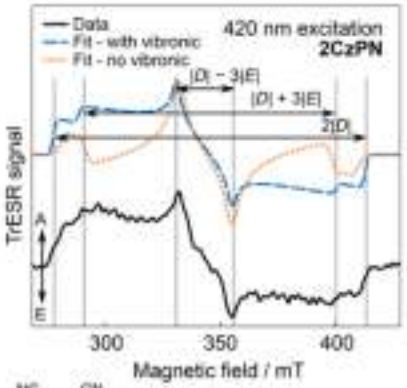
Prior Studies

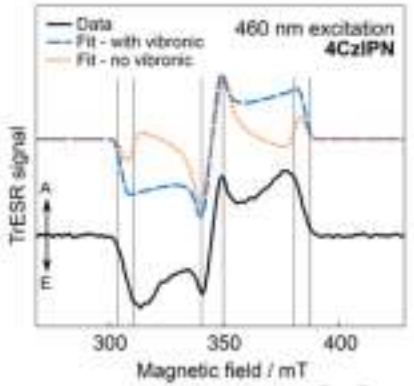


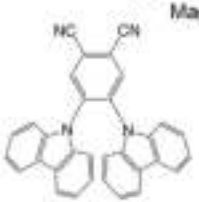
NI-N-PTZ



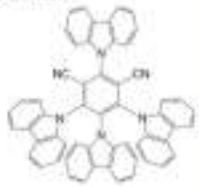
J. Phys. Chem. C, 2019, 123, 30171–30186; doi: 10.1021/acs.jpcc.9b09335

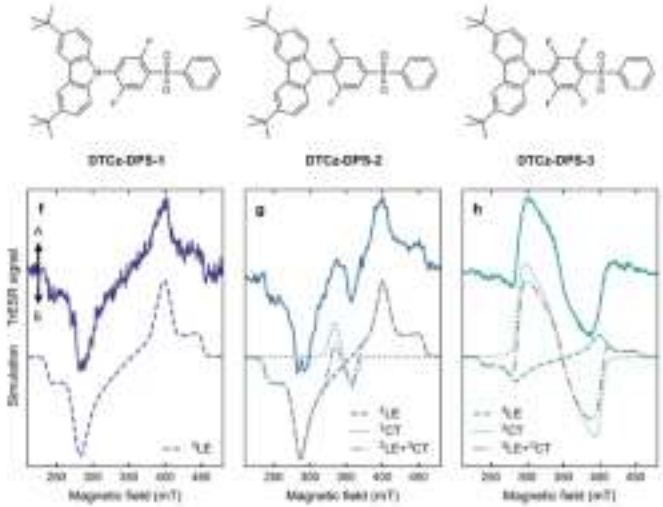






J. Phys. Chem. Lett. 2018, 9, 4053–4058; doi: 10.1021/acs.jpclett.8b01556

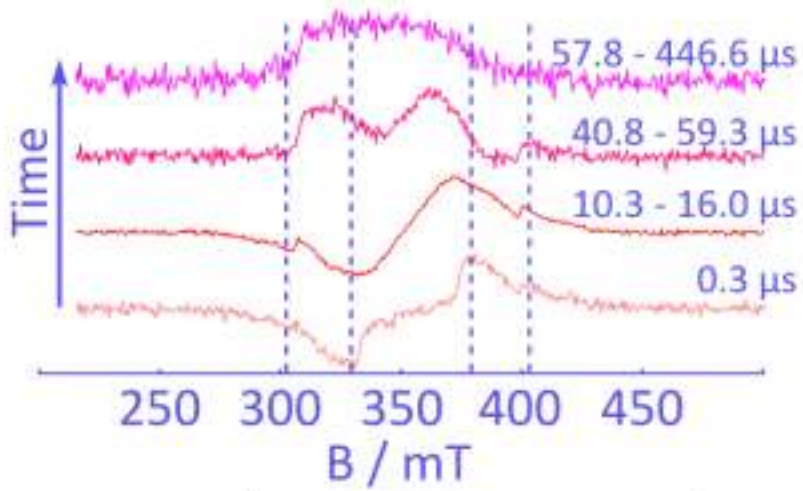


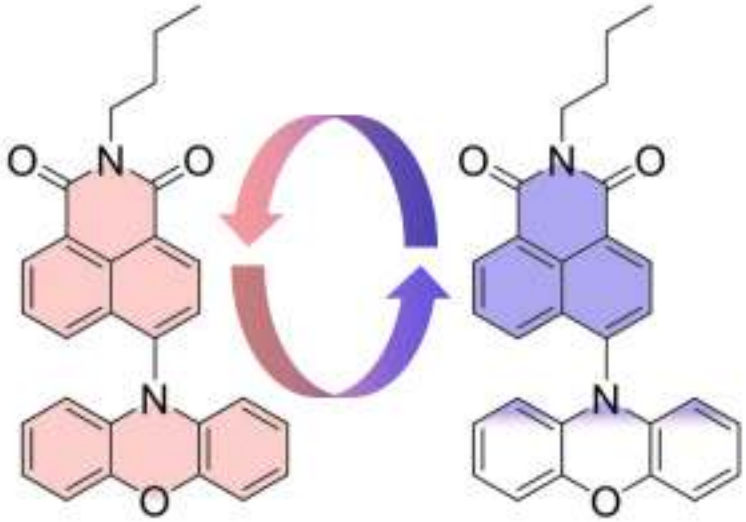


JNat. Commun., 2021, 12, 4532; doi: 10.1038/s41467-021-24612-9

- ✓ We were not the first to use TREPR for TADF OLED materials study
- ✓ There were groups before us

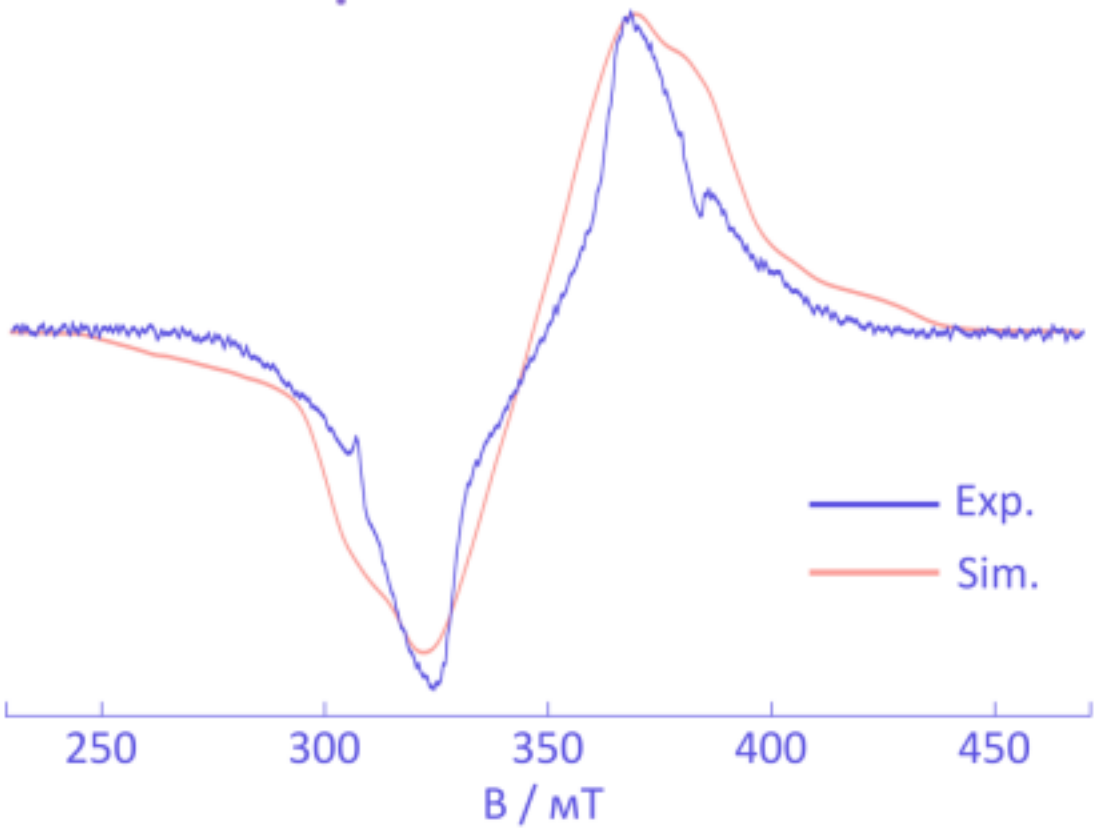
Concluding Remarks





- ✓ TR EPR reveals ^{3}LE-^{3}CT exchange in a TADF dyad NI-PXZ for the first time
- ✓ TR EPR is an important tool for the TADF OLED materials study

TR EPR spectra simulation. Full model



- ✓ We continue to work on ^{3}LE-^{3}CT exchange spectra interpretation

$$I_{ij} \sim Im\{\frac{[2k + R - i\Delta\omega_{ij}]}{(k + R - i\Delta\omega_{ij}^1)(k + R - i\Delta\omega_{ij}^2)}(\rho_{ii} - \rho_{jj})\}$$

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R - spin relaxation; $\Delta\omega_{ij}$ - constant resonance offset; $\Delta\omega_{ij}^x$ - offsets of the exchanging lines; k - exchange rate; ρ_{ii} - i-sublevel population

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- prof. Z. Zhao

- prof. Matvey Fedin

- prof. Jianzhang Zhao
- Xue Zhang
- Xiao Liu
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Thank you
For Your Attention!