B9 Thin film investigations on ferroelectric organic charge transfer systems

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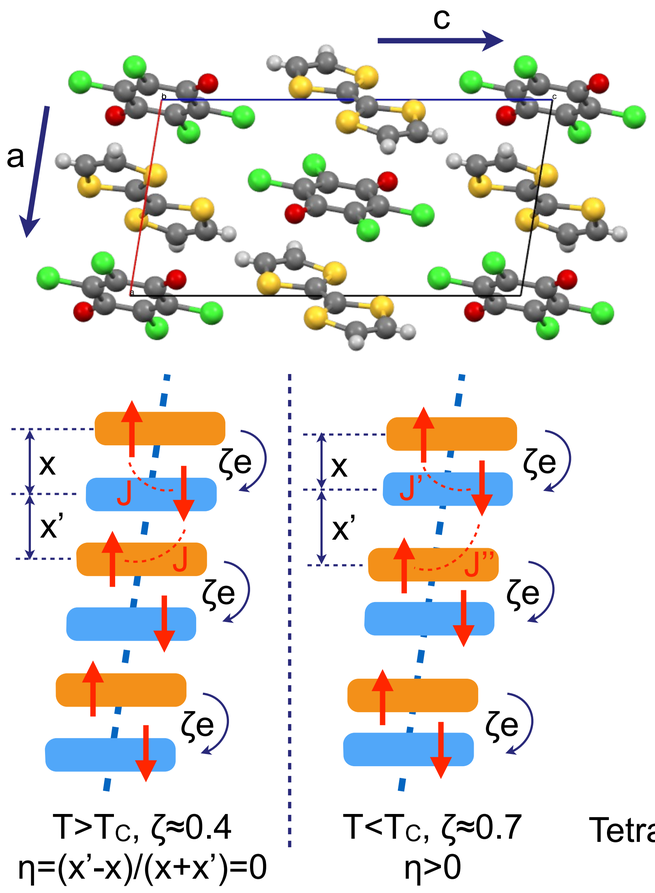
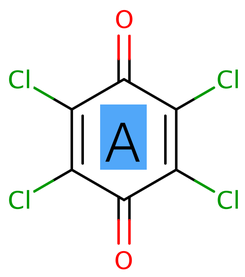
Introduction



- Neutral-ionic transition @ T_C=81 (bulk)
- Ferroelectric with large electronic contribution
- Strong pressure dependence of T_C (bulk)
- Dimerized spin chain (Spin-Peierls effect)

TTF
Tetrathiafulvalene



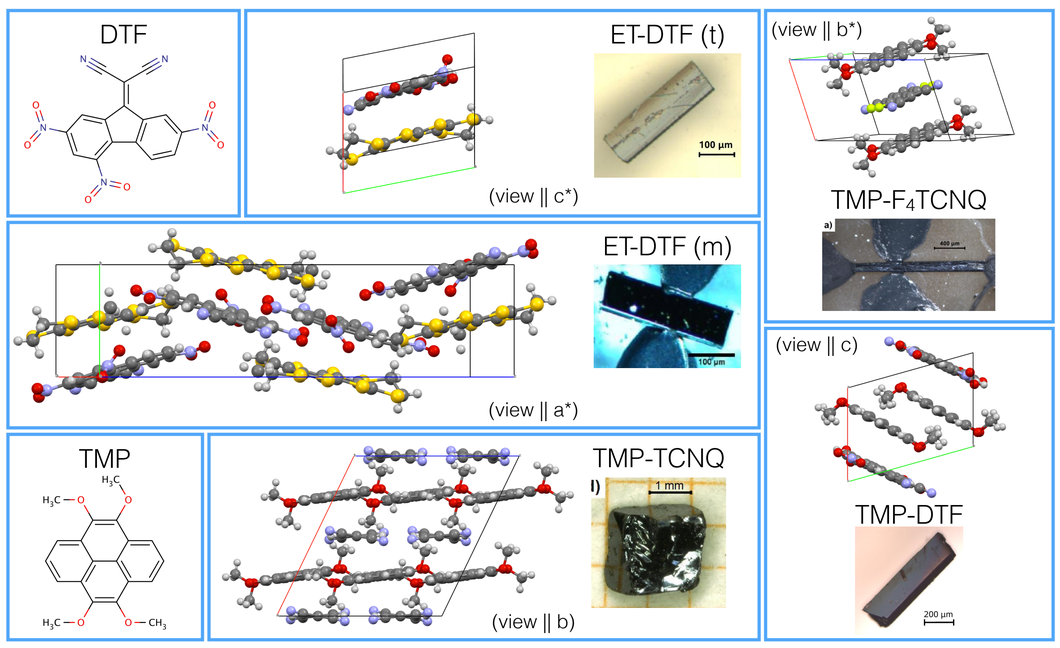
QCl$_4$
Chloranil

Research questions

- Influence of anisotropic strain on NI-transition (thin films)? B2
- Coupling of ferroelectric polarization on dimerized spin state?
- Magnetic ground state of spin-chain under strain and exchange bias coupling to ferromagnetic nanostructures?
- Domain structure
  - Slow dynamics of charged domain walls (solitons)? B11
  - Domain size and orientation? B8

New mixed stack organic CTS

Achievements B2 B10



Overview of key properties

CTS	ζ exp.	ζ th.	SG	PS	$\sigma\,[Scm^{-1}]$	$E_A\,[eV]$	$\Delta E\,[eV]$	$E_g\,[eV]$
TMP–TCNQ	0.14	0.13	C2/c (15)	centrosym.	$< 10^{-11}$	-	0.5–0.7	0.35
TMP–F$_4$TCNQ	0.12	0.20	P$\bar{1}$ (2)	centrosym.	$\approx 10^{-7}$	0.96	0.0–0.3	0.26
ET–DTF(m)	0.19	0.78	P21/n (14)	centrosym.	$\approx 10^{-5}$	0.34	0.5–0.7	0.047
ET–DTF(t)	≈ 0.21	0.91	P1 (1)	polar	$\approx 10^{-7}$	0.30	0.5–0.7	0.026
TMP–DTF	0.14	0.08	P$\bar{1}$ (2)	centrosym.	$\approx 10^{-5}$	0.06	0.7–1.0	0.7
TTF–QCl$_4$(N)	0.2	-	P21/n (14)	centrosym.	$\approx 10^{-5}$	0.13	≈ 0.3	≈ 0.06
TTF–QCl$_4$(I)	0.6	-	Pn (7)	polar	-	≈ 0.08	≈ 0.3	≈ 0.08

ζ: charge transfer in units of e from IR-spectroscopy (exp.) and from ab initio DFT calculations (th.), SG: space group, PS: point symmetry, σ: room temperature conductivity, E_A: transport activation energy, ΔE: redox-potential of DA-pair, E_g: band gap from DFT calculations.

TMP-(F$_4$)TCNQ

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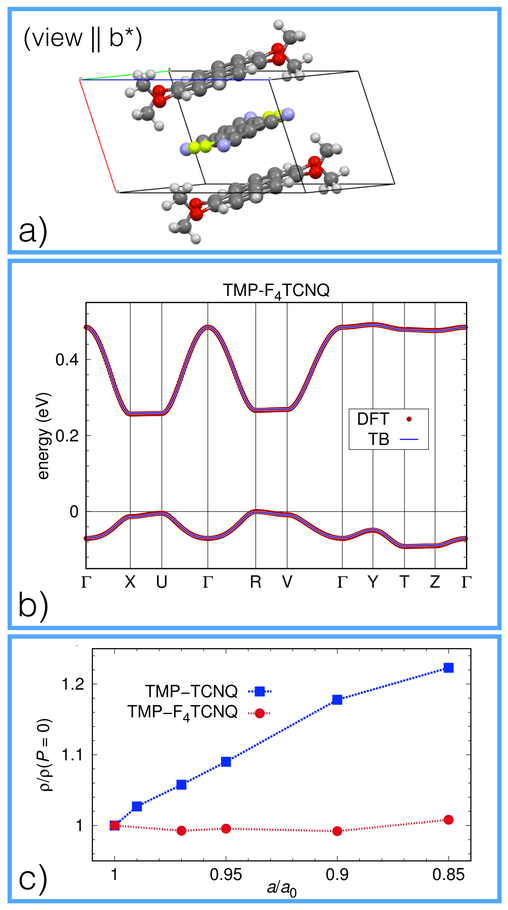
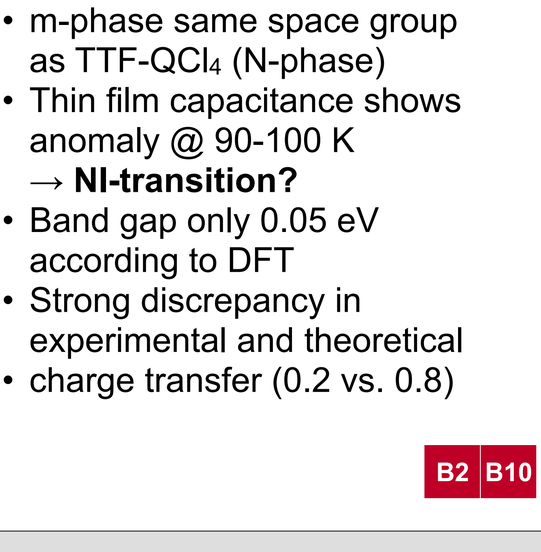
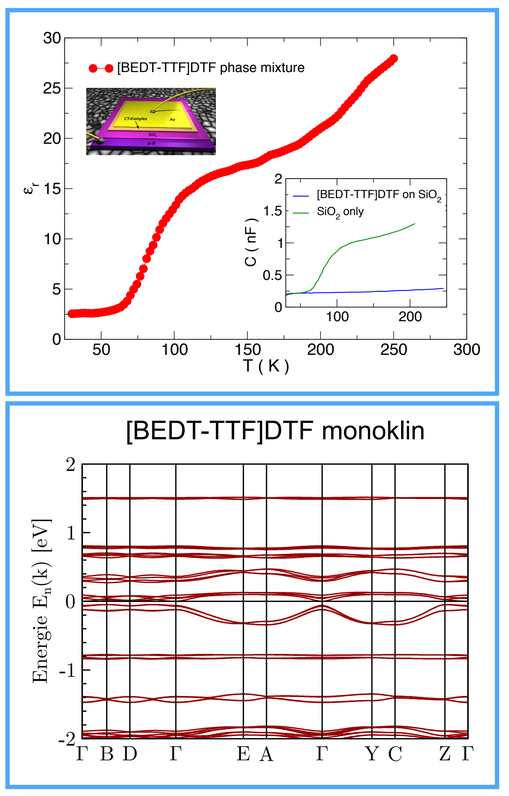


- TMP-F$_4$TCNQ has virtually ideal geometrical D-A overlap
- Weak charge transfer (ζ≈0.1)
- No indication for NI-transition
- Simulated uniaxial pressure along stacking axis (DFT):
  - Strong effect for TMP-TCNQ
  - No effect for TMP-F$_4$TCNQ

Comparison of charge distribution



[BEDT-TTF]DTF

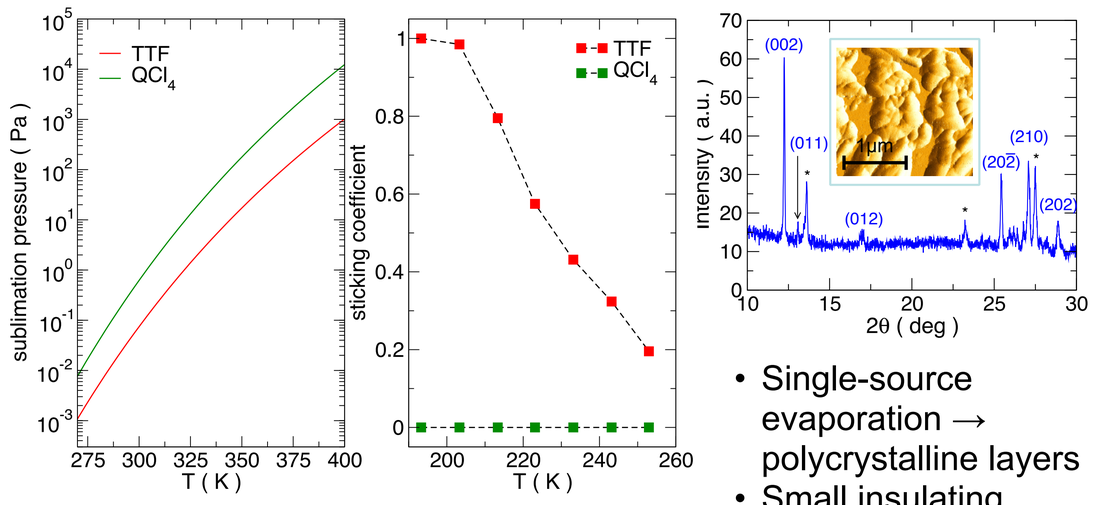


- [BEDT-TTF]DTF crystallizes in two structures (**t**riclinic, **m**onclinic)
- Thin films grow mixed-phase
- Low-temperature XRD shows no evidence for structural transition in t-phase
- m-phase same space group as TTF-QCl$_4$ (N-phase)
- Thin film capacitance shows anomaly @ 90-100 K → **NI-transition?**
- Band gap only 0.05 eV according to DFT
- Strong discrepancy in experimental and theoretical
- charge transfer (0.2 vs. 0.8)

B2 B10

TTF-QCl$_4$ thin film growth

Achievements



- Very small sticking coefficients
- Growth below T_{sub} = 200 K allows good control of rate
- Single-source evaporation → polycrystalline layers
- Small insulating impurity phase contribution
- Island growth