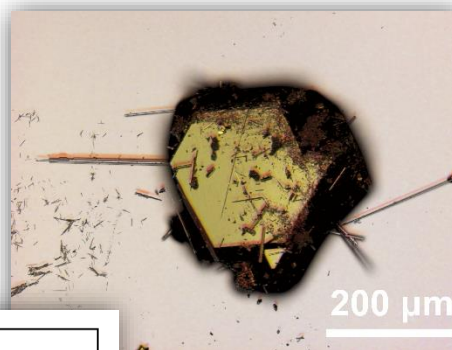
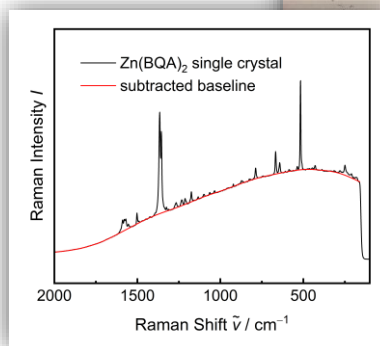
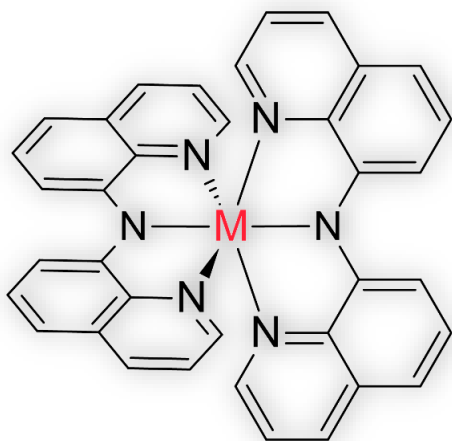




Structure Characterization of Bis-(bis(8-quinolinyl)amide) Zinc and Iron Complex Thin Films

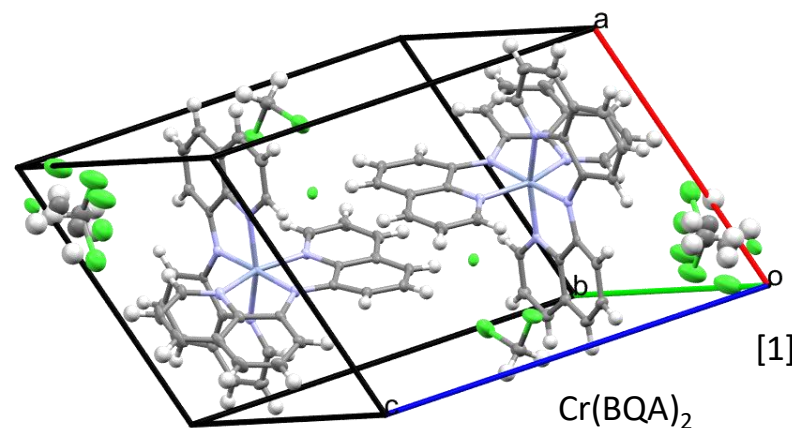
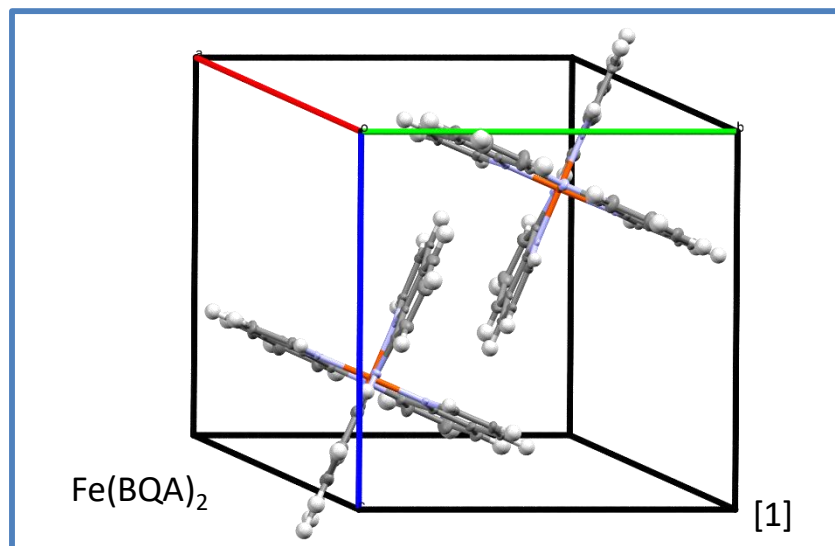
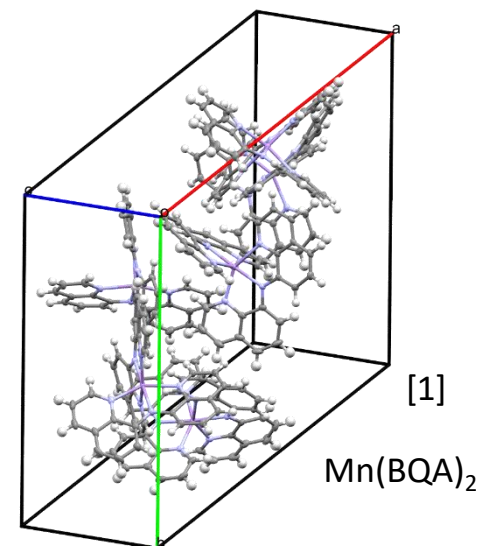
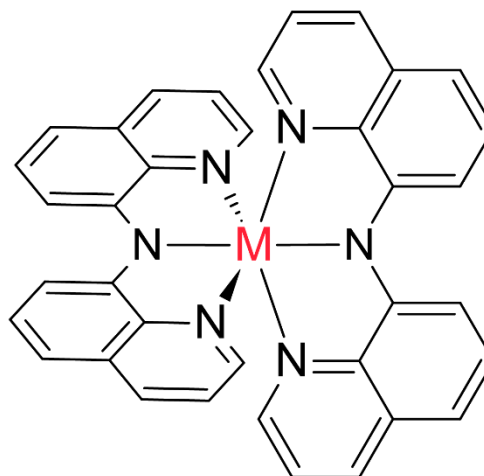
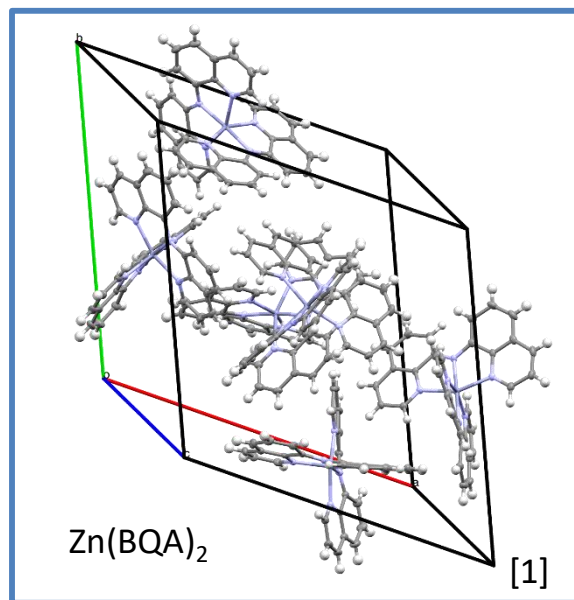
Vertiefungsmodul – Physical Chemistry and Material Science

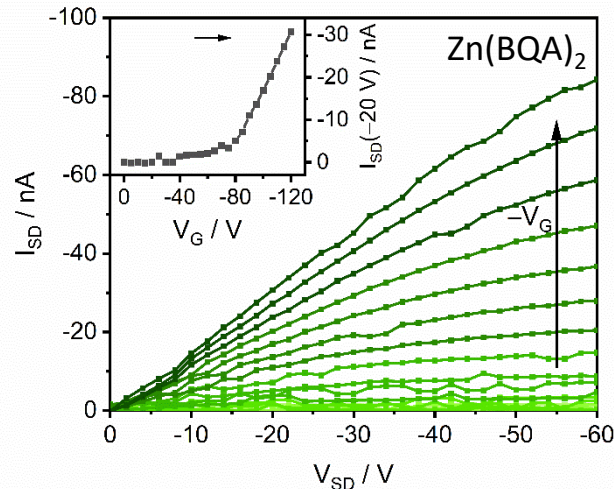
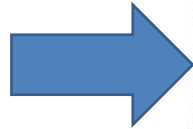
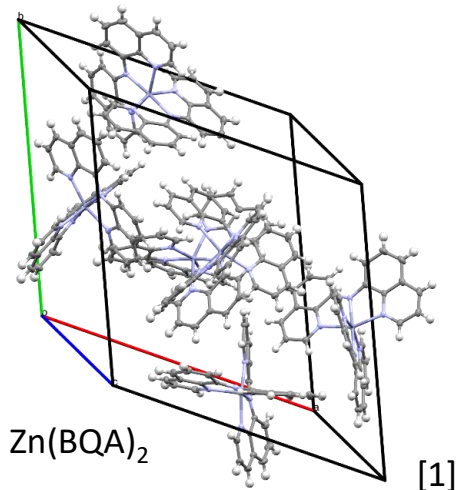
Pascal Schweitzer

Institut für Angewandte Physik, Justus-Liebig-Universität Gießen

5 January 2021

Gießen



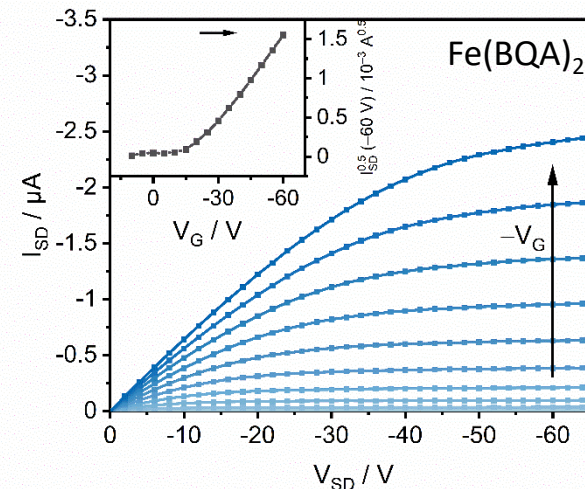
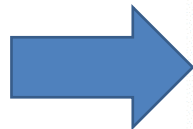
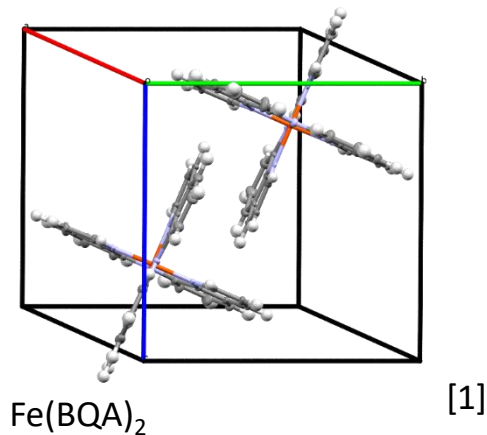


charge carrier mobility

$$\mu_{\text{lin}}(-20 \text{ V}) = 9.5 \times 10^{-7} \frac{\text{cm}^2}{\text{Vs}}$$

on-off-ratio of the device current

$$\frac{I_{\text{on}}}{I_{\text{off}}} = 15$$



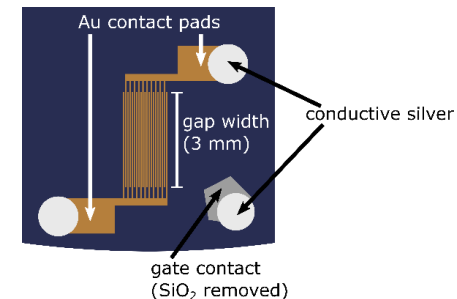
$$\mu_{\text{sat}}(-60 \text{ V}) = 8.1 \times 10^{-5} \frac{\text{cm}^2}{\text{Vs}}$$

$$\frac{I_{\text{on}}}{I_{\text{off}}} = 1178$$

single crystal

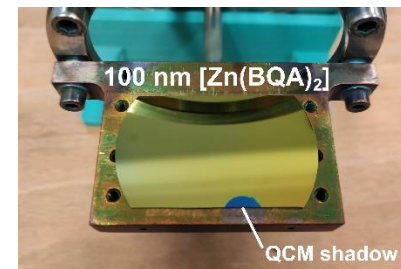
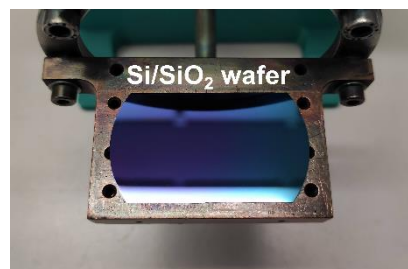
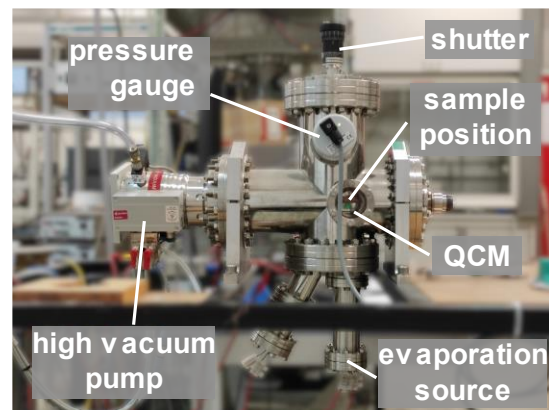
connection?

thin film transistor



1. Can we **exclude morphology effects as an influence** to the device performance?
 - grain size, grain uniformity, grain boundaries, homogeneity of the film, pin holes and cracks
2. Can we **exclude decomposition** of the compounds during film preparation?
3. Is the **single crystalline structure prevalent in the film**?

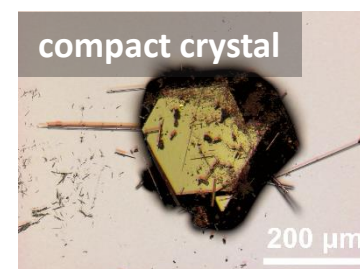
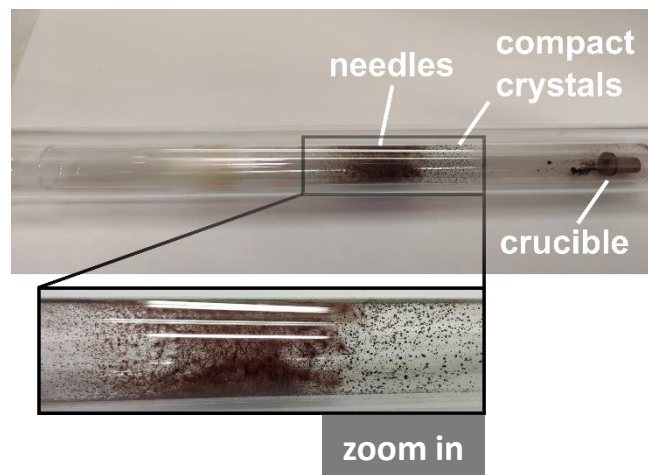
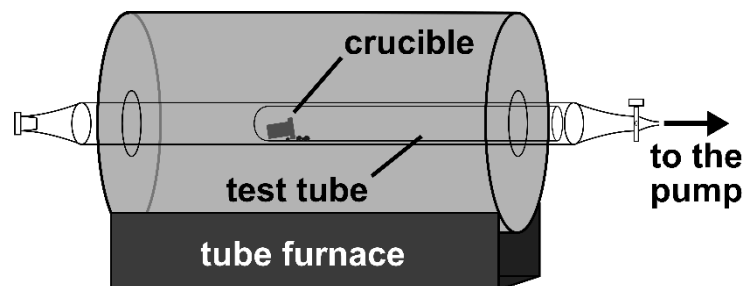
Thin Film Preparation by Physical Vapor Deposition



- **high vacuum:** $p \leq 5.4 \times 10^{-6}$ mbar
- resistively heated BN crucible
- evap. rate: $r = 0.5 \pm 0.2$ nm min⁻¹
- film thickness: $57 \text{ nm} \leq d \leq 103 \text{ nm}$

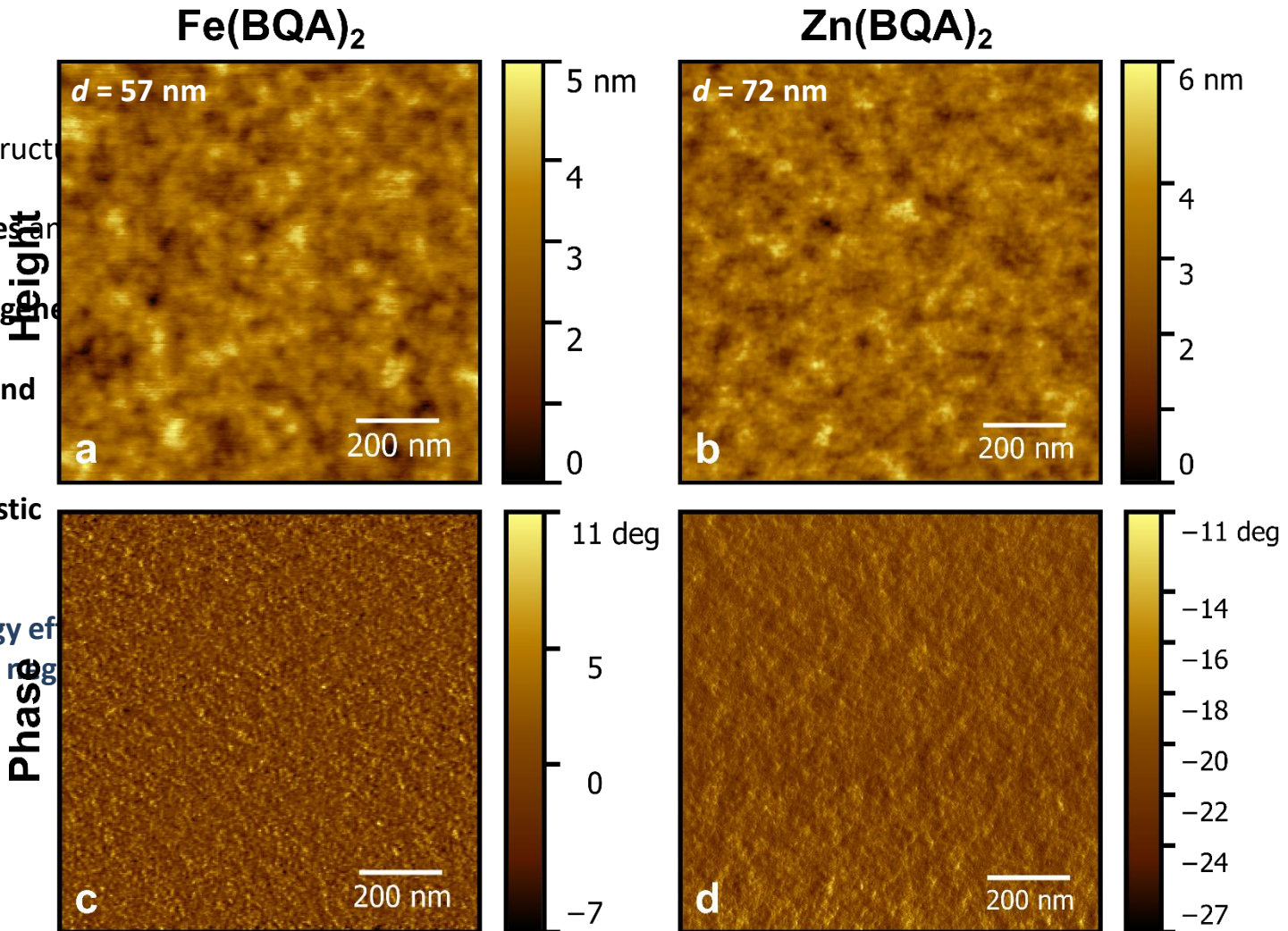
Single Crystal Growth by Vacuum Sublimation

- **no air contact – no degradation**
- crystals **free of solvent molecules**
- **fine vacuum:** $p \approx 1 \times 10^{-1}$ mbar
- temperature: $250 \text{ }^{\circ}\text{C} \leq \vartheta \leq 270 \text{ }^{\circ}\text{C}$
- duration: 5 days



1. Can we **exclude morphology effects as an influence** to the device performance?
 - grain size, grain uniformity, grain boundaries, homogeneity of the film, pin holes and cracks
2. Can we **exclude decomposition** of the compounds during film preparation?
3. Is the **single crystalline structure prevalent in the film**?

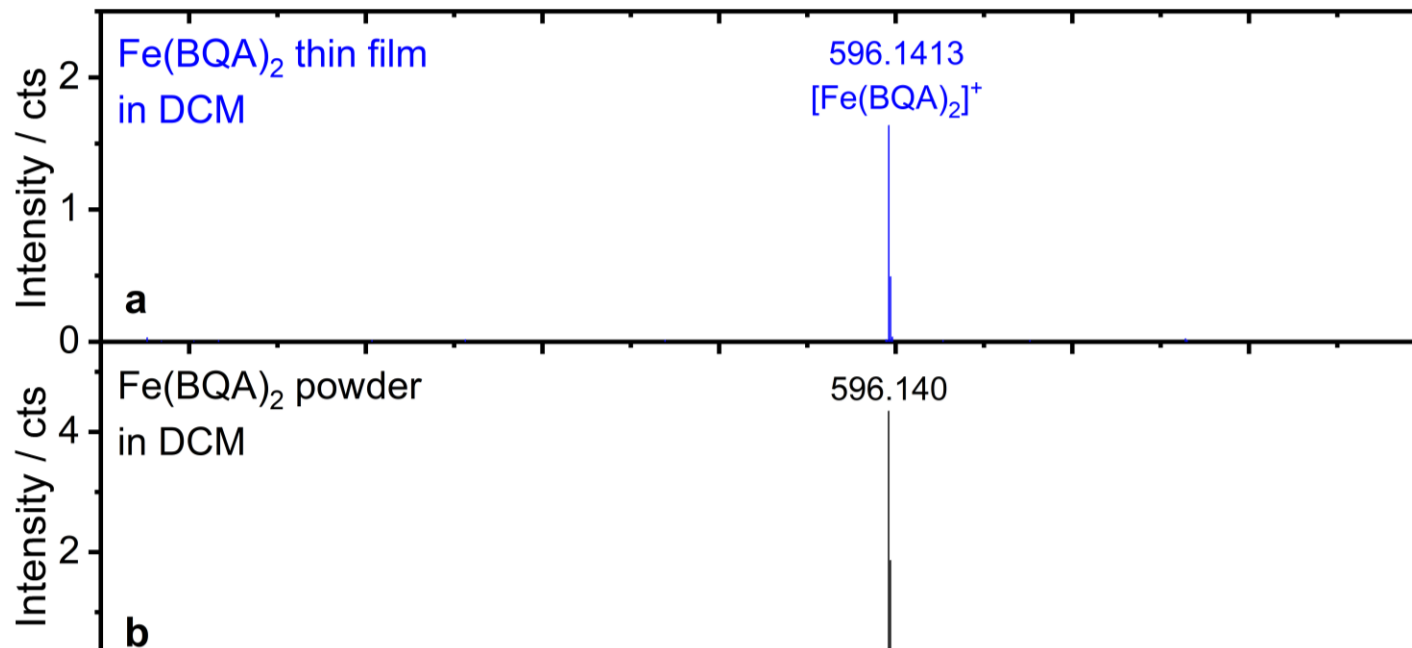
- granular structure
- no pin holes
- high homogeneity
- similar island sizes
- similar elastic properties
- morphology effects apparently negligible



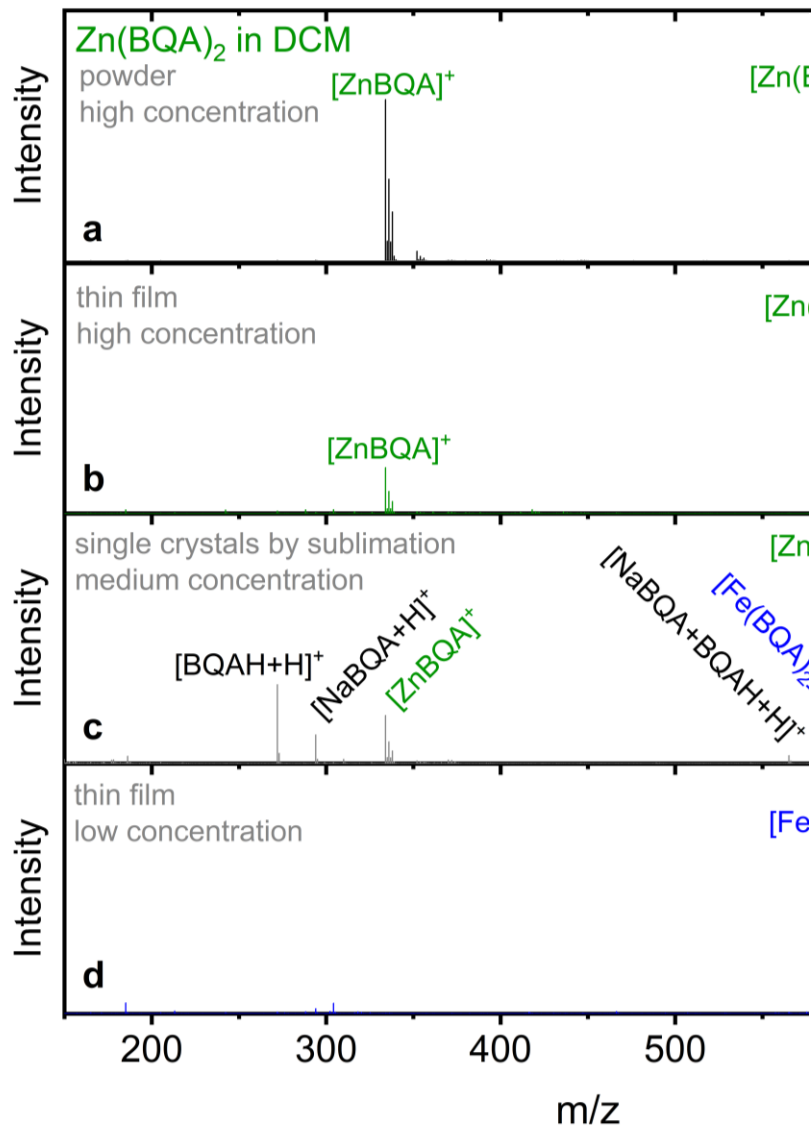
1. Can we **exclude morphology effects as an influence** to the device performance?
✓ **Yes, morphological differences of the films can be neglected.**

2. Can we **exclude decomposition** of the compounds during film preparation?

3. Is the **single crystalline structure prevalent in the film?**



- **expected m/z ratio found:** $m/z = 596,14$
- **isotope signals** at 594.14, 597.14, 598.14
- **no fragmentation**
- **similar signals**
- **no decomposition during PVD process** → suitable technique for film preparation

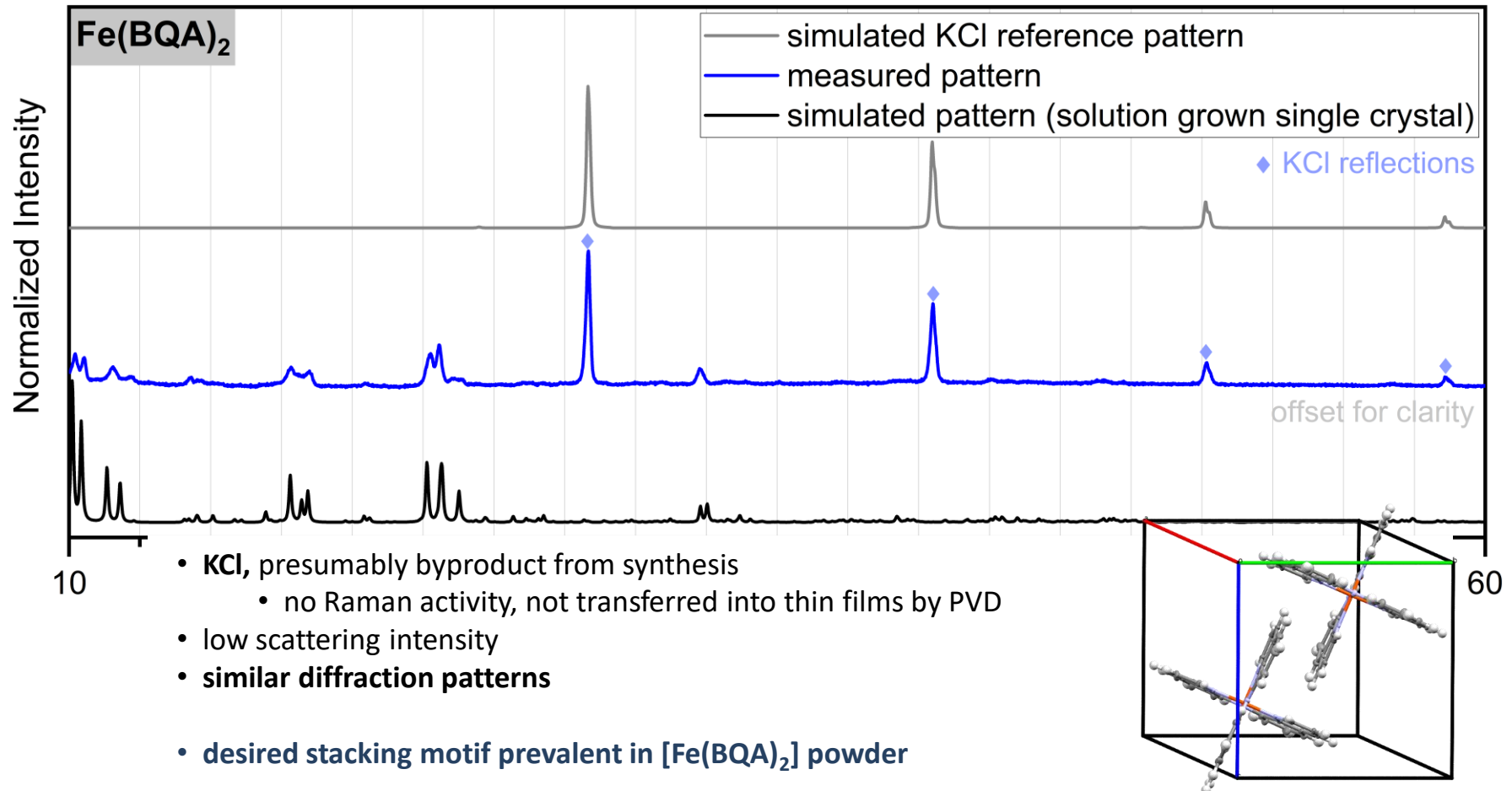


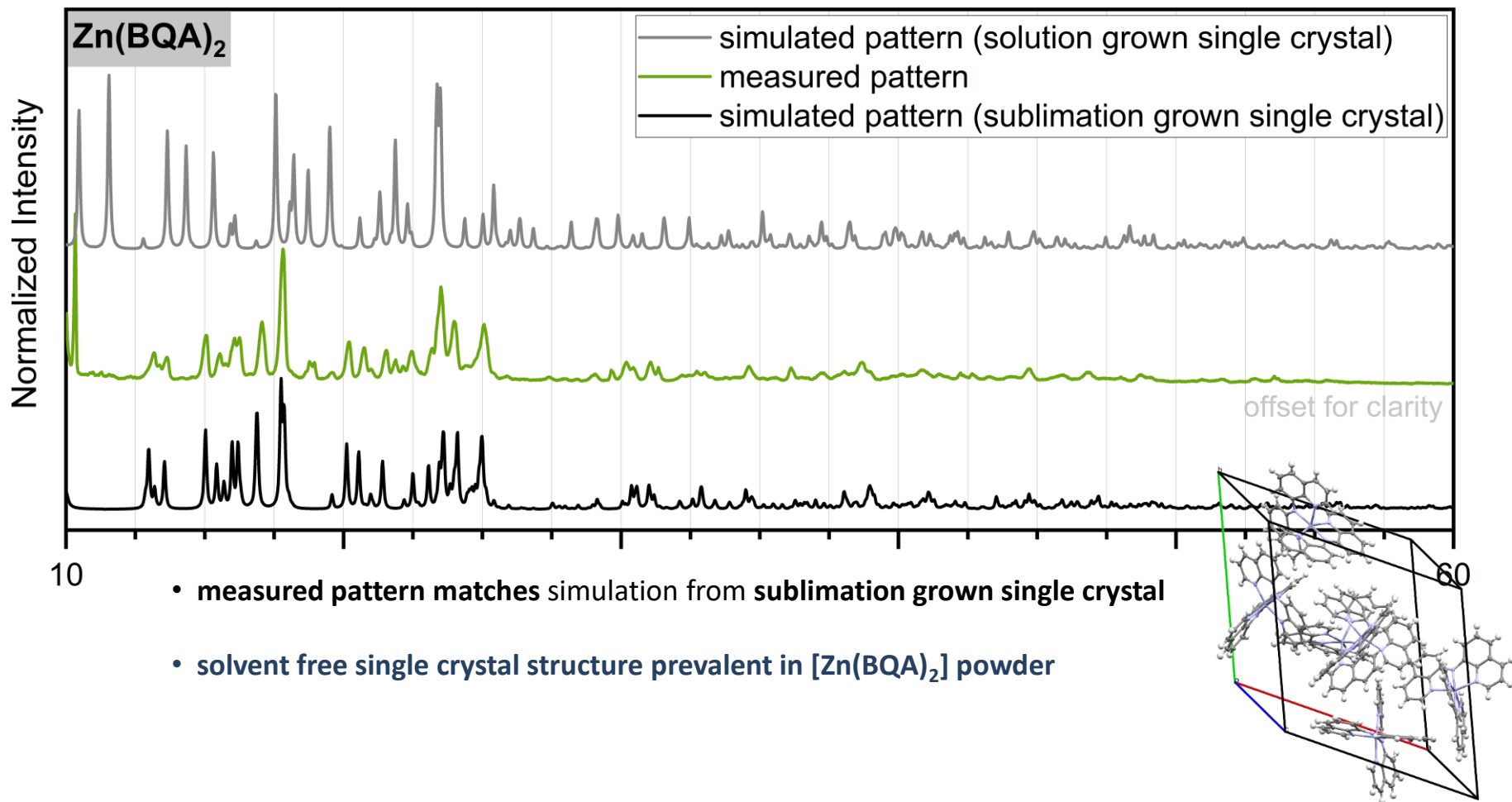
- **powder**, high concentration:
 - adduct with hydrogen
 - fragment (splitting-off BQA)
- **thin film**, high concentration:
 - powder signals
- **single crystal**, medium concentration:
 - no fragments found by XRD
 - powder signals
 - additional fragments & adducts
 - weak [Fe(BQA)₂]⁺ signal (!)
- **thin film**, low concentration:
 - dominant [Fe(BQA)₂]⁺ signal
 - *attempted explanation*:
DCM hydrolysis; HCl forms FeCl₂ at contact to metal cannula; complete conversion of the small amount of [Zn(BQA)₂] to [Fe(BQA)₂]
- no decomposition during PVD process
→ suitable technique for film preparation

1. Can we **exclude morphology effects as an influence** to the device performance?
✓ Yes, morphological differences of the films can be neglected.

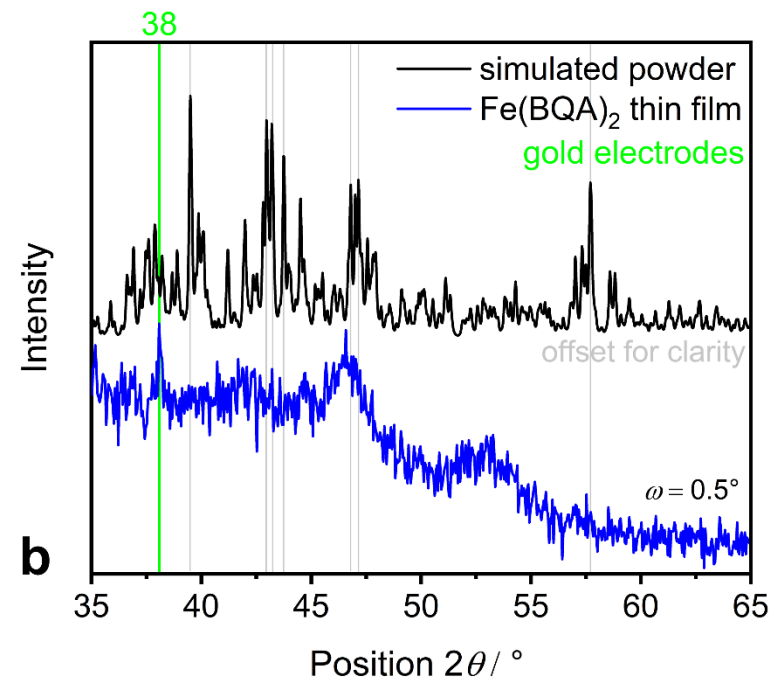
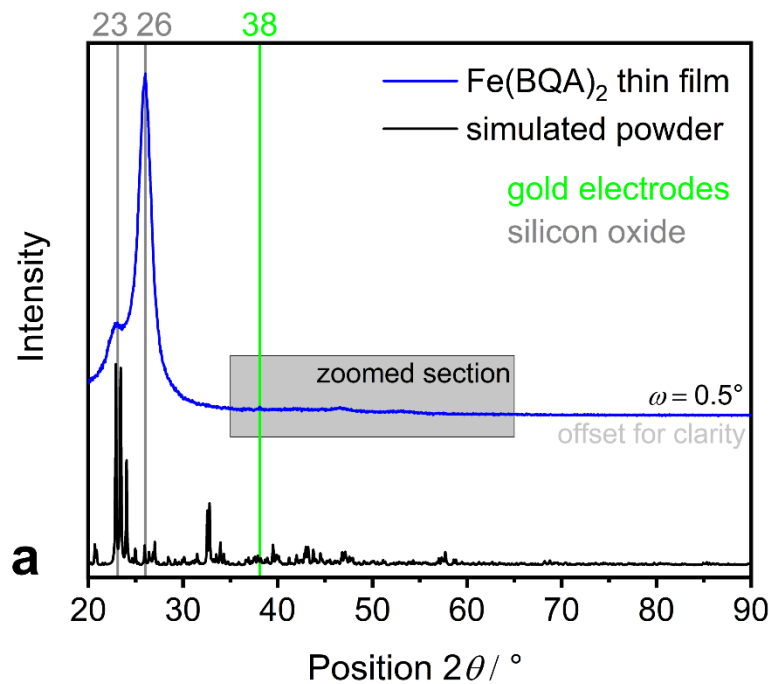
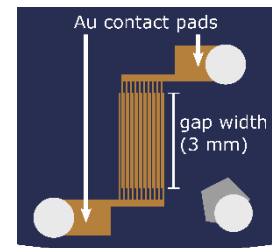
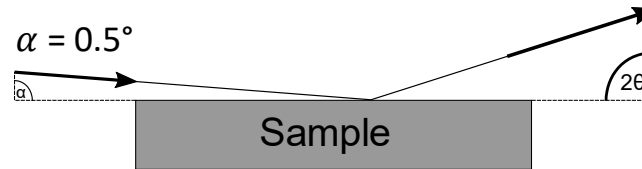
2. Can we **exclude decomposition** of the compounds during film preparation?
✓ Yes, PVD is suitable for thin film preparation without decomposition.

- 3. Is the **single crystalline structure prevalent** in the film?

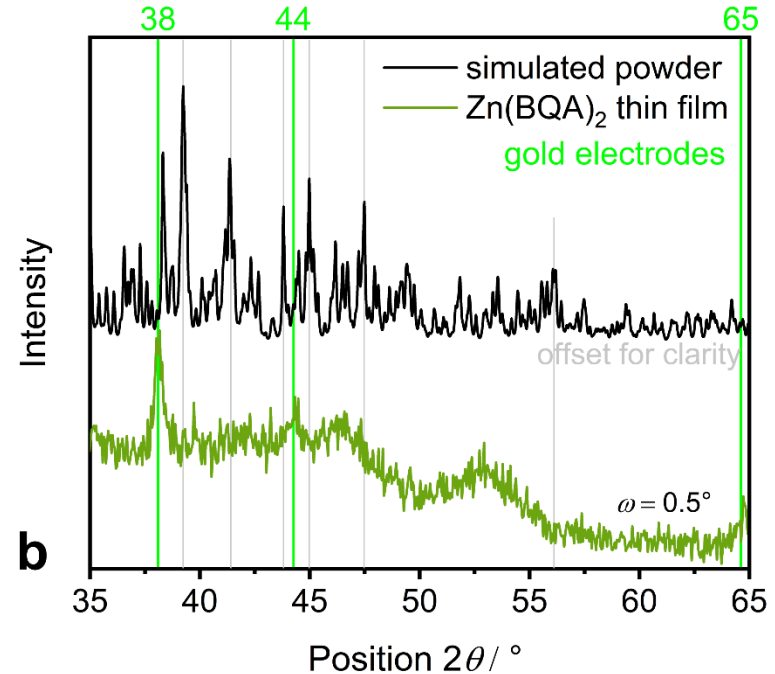
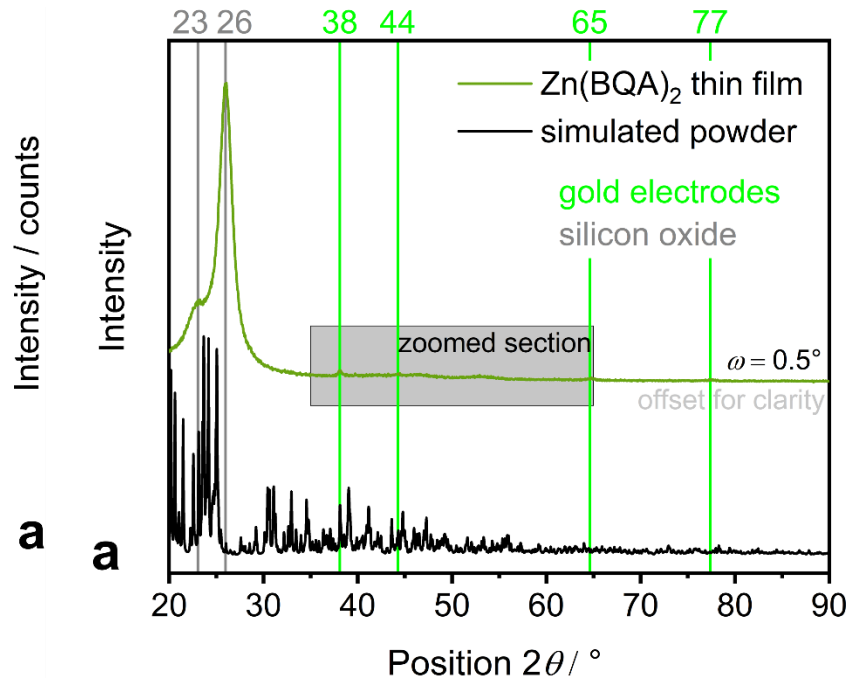
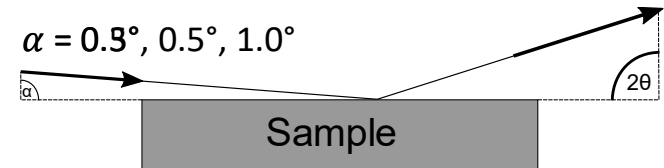




- **0.5° incidence angle:** probing the topmost sample layers
- analysis performed in **device geometry**
- film thickness: **57 nm**
- strong **substrate reflexes**
- **no complex specific reflexes**

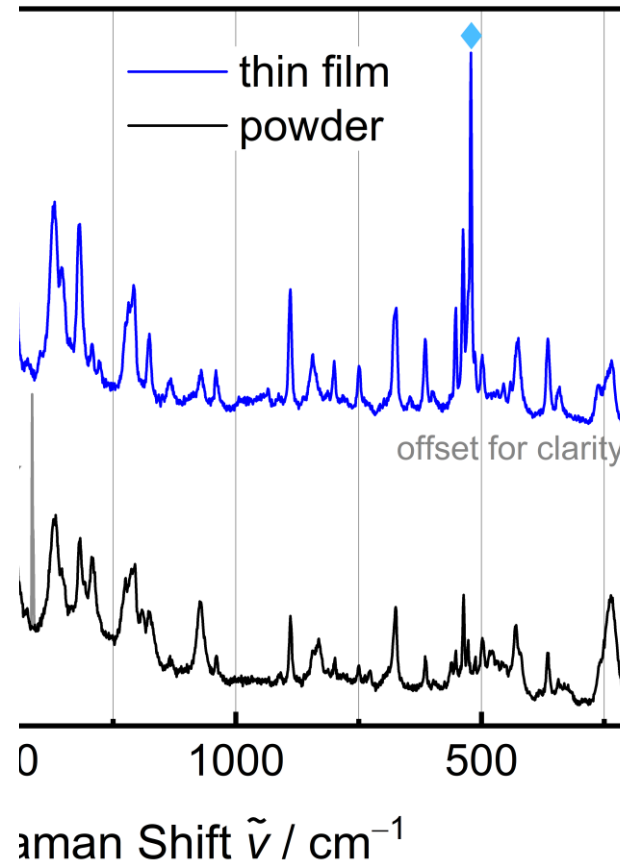


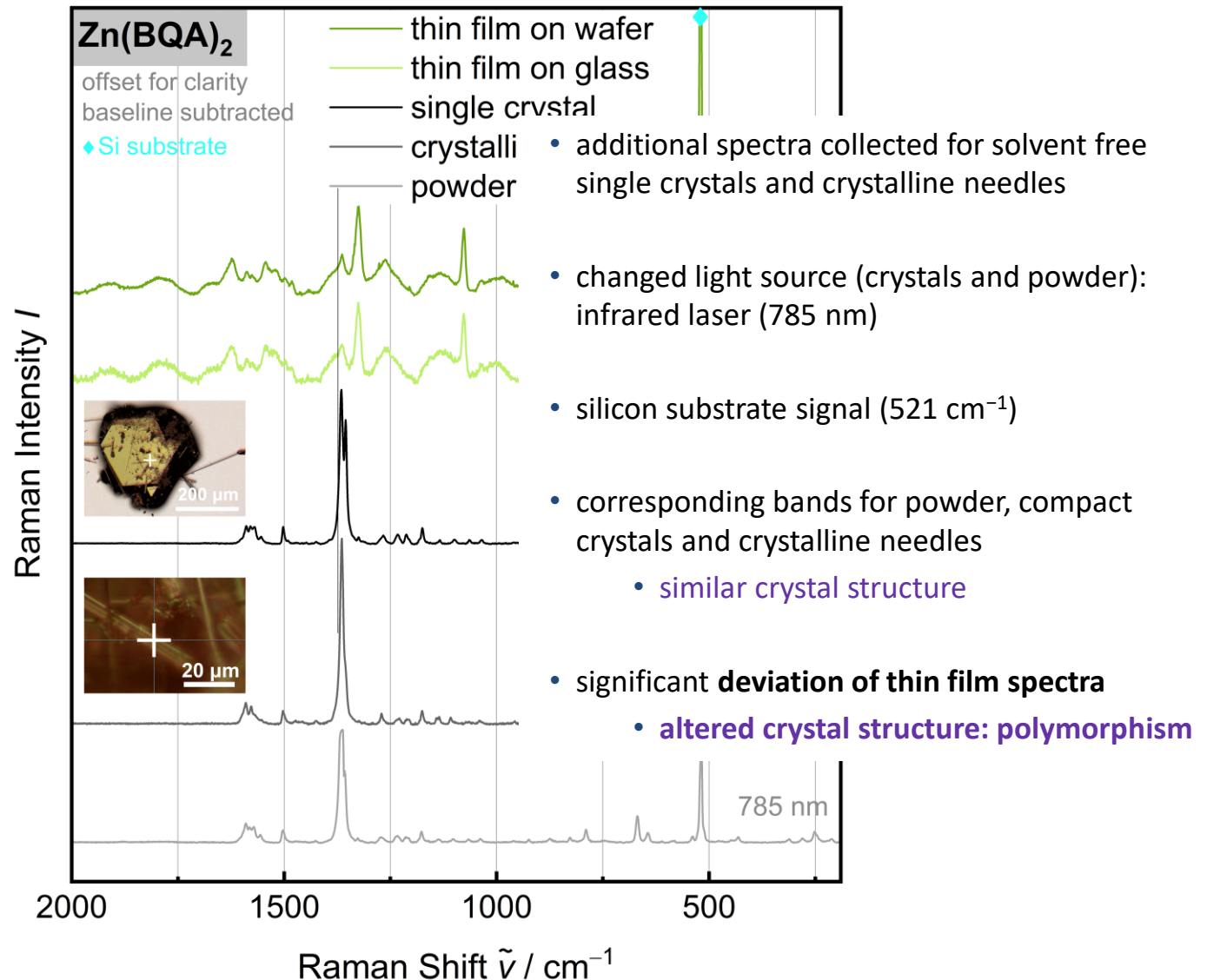
- **increased film thickness** (100 nm)
- **substrate reflexes** comparable to $[\text{Fe}(\text{BQA})_2]$
- **no complex specific reflexes**



- variation of: **incidence angle**, **integration time** per data point, film **thickness**, **substrate**
- **crystal structure of BQA complex thin films not accessible through GI-XRD**

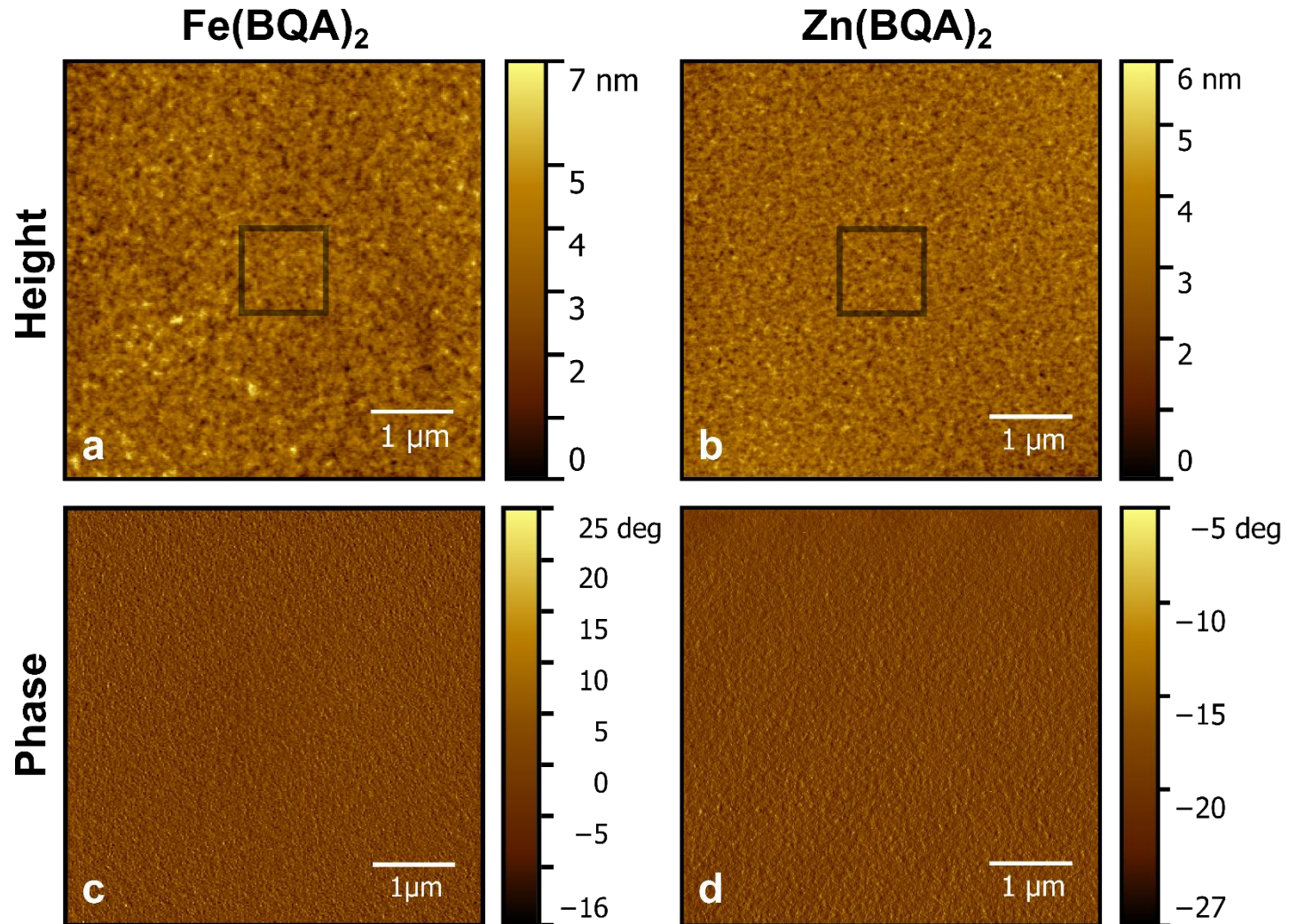
- comparing **vibrational properties in solid state**
 - sensitivity for **changes of the crystalline order** of organic semiconductors
- irradiation of the sample: red laser, 633 nm.
- silicon substrate signal (521 cm^{-1})
- cosmic rays event ($1416\text{--}1411\text{ cm}^{-1}$)
- corresponding Raman bands
- **similar vibrational properties and crystalline order** of thin films and powder
- **successful transfer of the stacking motif into thin film devices**

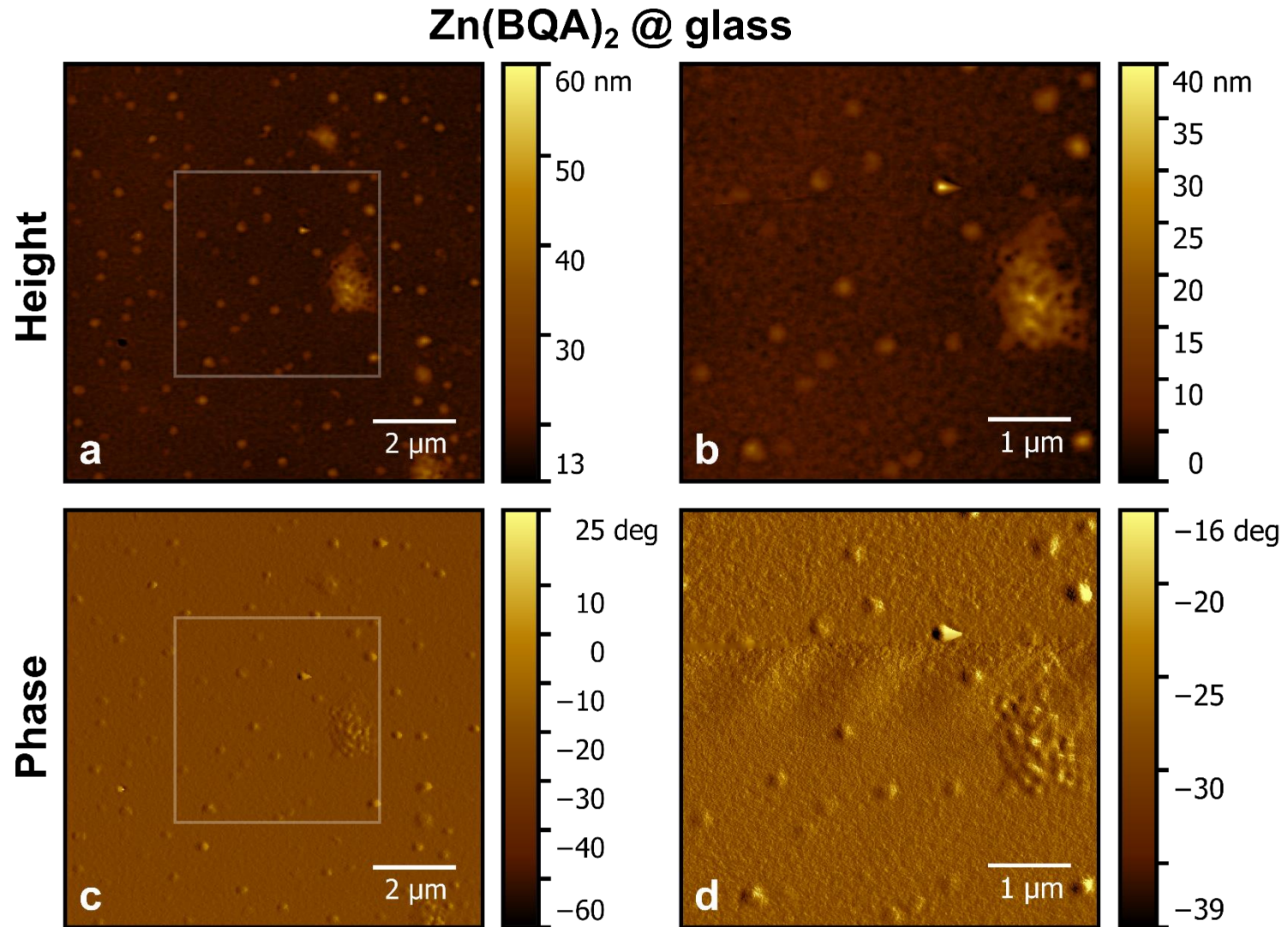


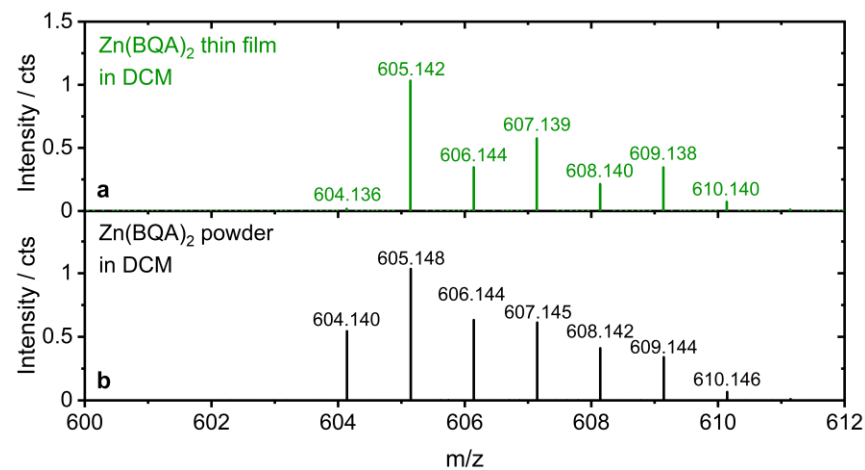
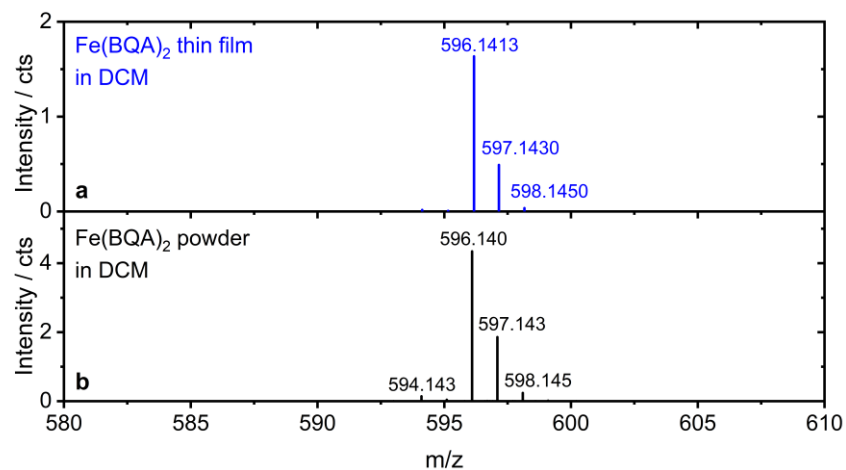
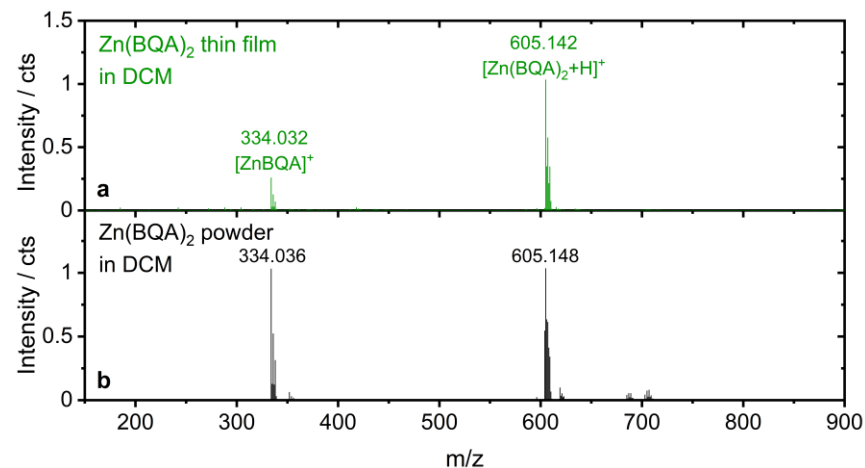
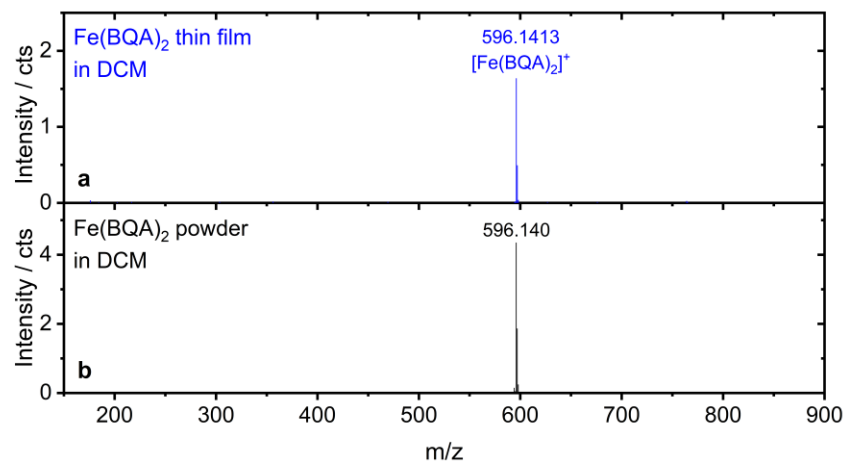


1. Can we **exclude morphology effects as an influence** to the device performance?
✓ Yes, morphological differences of the films can be neglected.
2. Can we **exclude decomposition** of the compounds during film preparation?
✓ Yes, PVD is suitable for thin film preparation without decomposition.
3. Is the **single crystalline structure prevalent in the film**?
 - ✓ [Fe(BQA)₂]: **successful transfer of the beneficial stacking motif** into thin film devices → **efficient charge transport**
 - ✗ [Zn(BQA)₂]: **polymorphism**, presumably due to lower lattice energy and weak intermolecular interaction → **inefficient charge transport**

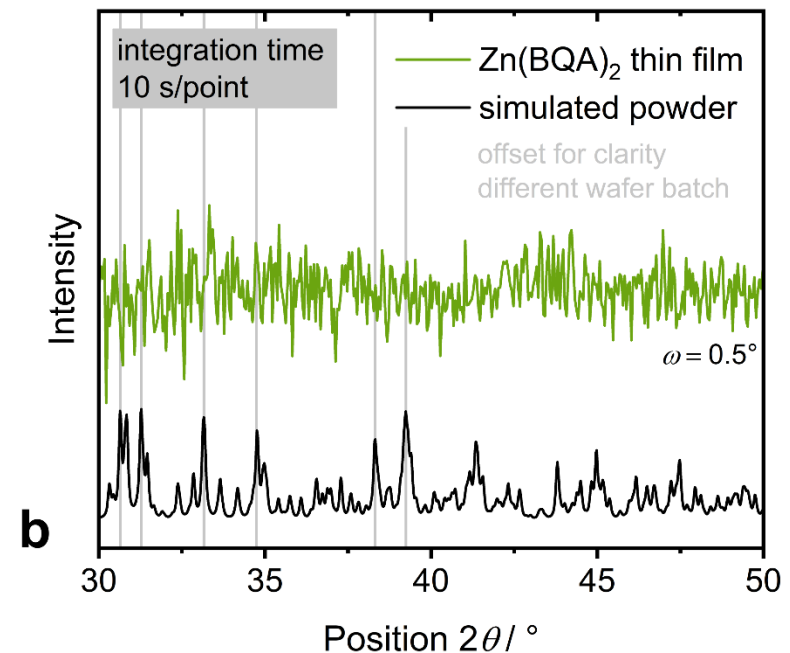
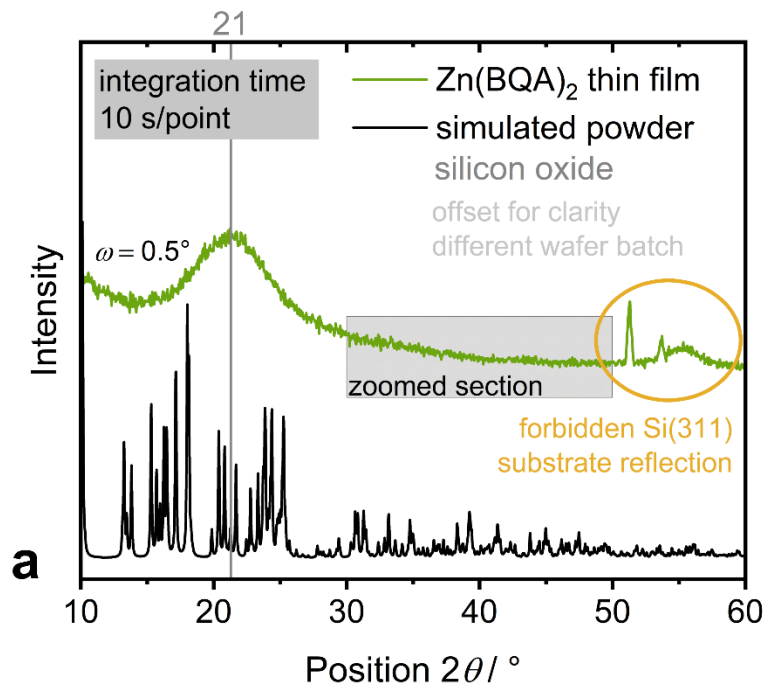
Questions and Discussion



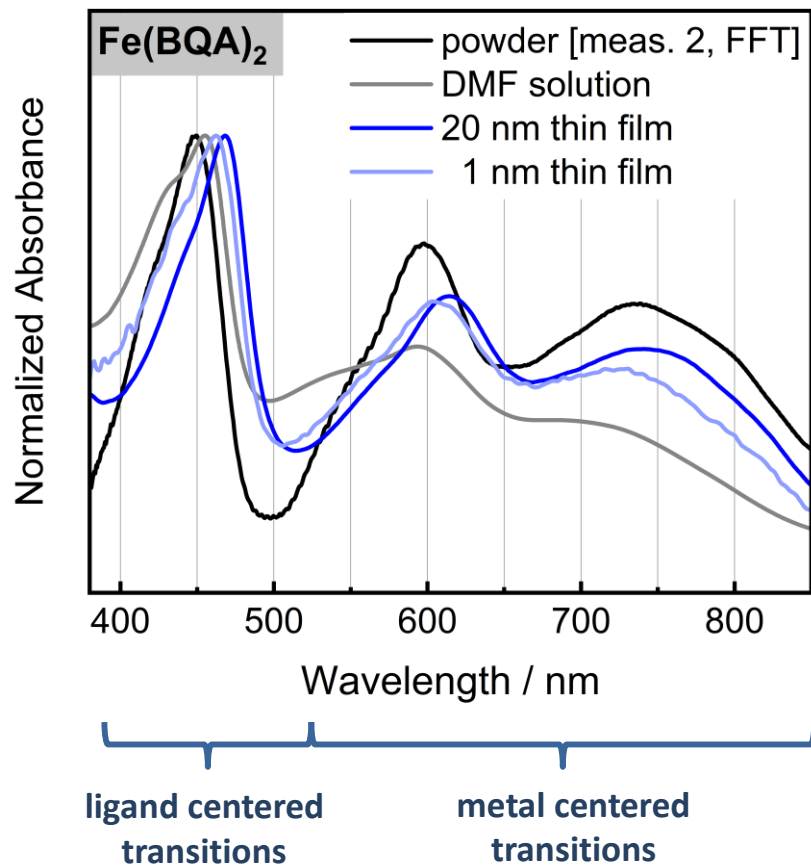




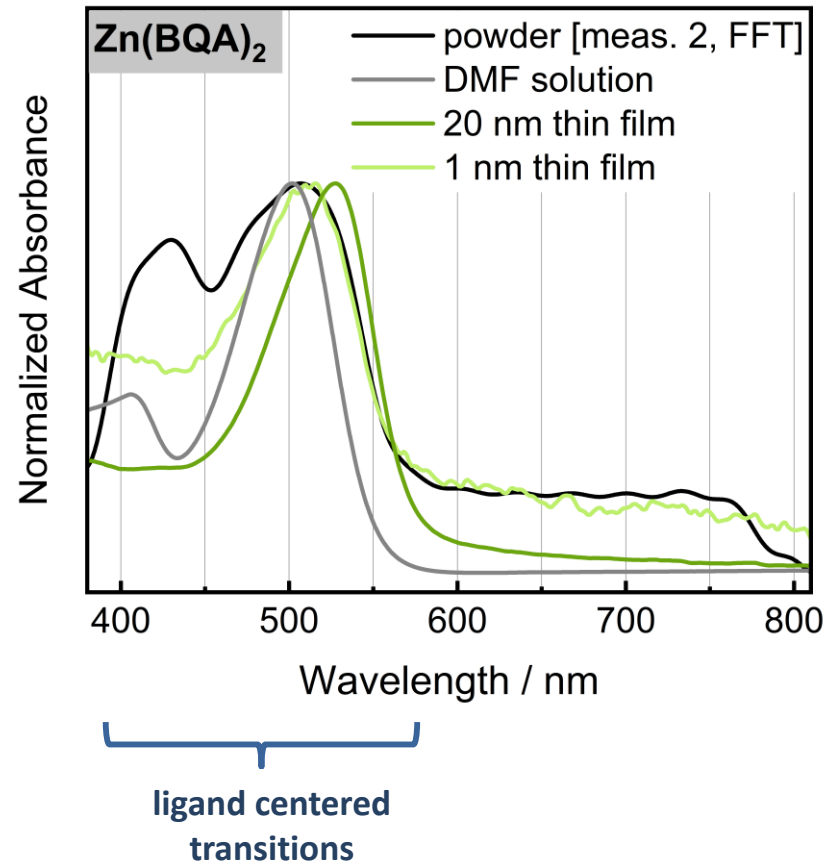
- **doubled integration time (10 s)**
- different wafer substrate (SiO_2 : α -cristobalite, not keatite)
- no gold microelectrode arrays
- **no correlation of simulated and measured pattern**



- **correlation of bands $\rightarrow$ stability** of $[\text{Fe}(\text{BQA})_2]$
- red shift during film growth
- powder and solution spectra blue shifted vs. film
 - **removal of solvent molecules during PVD**



- **correlation of bands $\rightarrow$ stability** of $[\text{Zn}(\text{BQA})_2]$
- red shift during film growth
- powder and solution spectra blue shifted vs. film
 - film: missing high energetic band (400-450 nm)
 - **crystal structure differences**



- comparison of thin films and powder Raman spectra of both complexes
 - **Some band positions correlate**, presumably due to **similar molecular structure**

