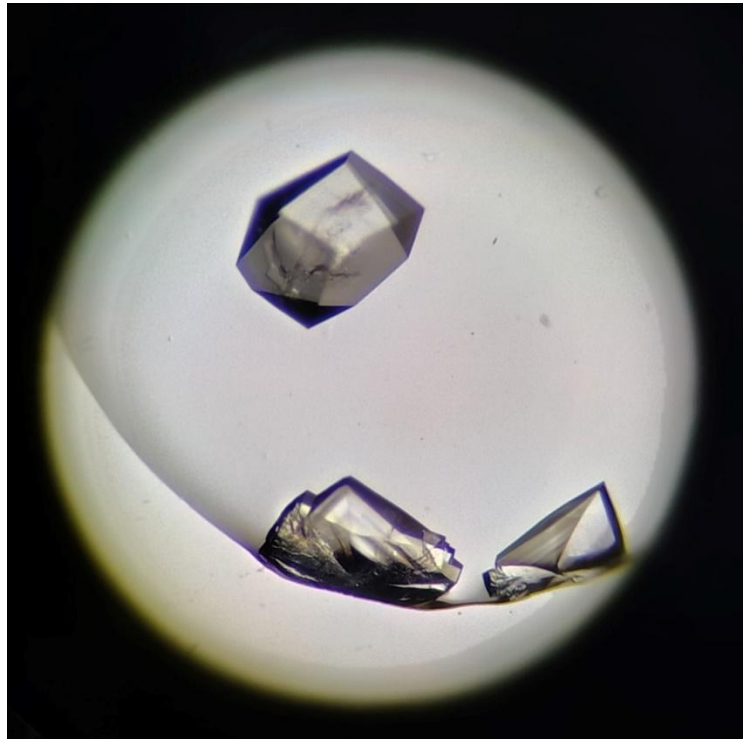


Flexpole

The research of flexible and polar crystals

PhD student Chiara Pizzo

"Gilberto Vlaic" XVIII School on Synchrotron Radiation: Fundamentals, Methods and Applications
21th September - 1st October 2026, Muggia (Italy)

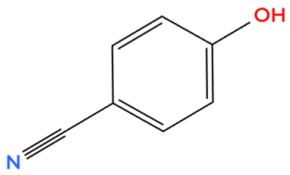
Introduction and aim

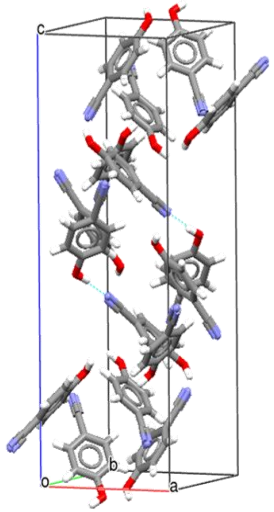
OSSCs (Organic Semiconducting Single Crystals) as materials for electronic devices.

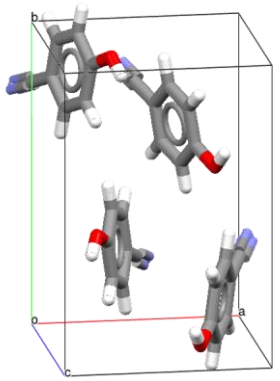
Key properties searched:

- **MECHANICAL FLEXIBILITY**
- **POLARITY** and **ANISOTROPIC CHARGE TRANSPORT**: crystal orientation, face indexing, and crystal packing allow us to determine the optimal crystal orientation for the electrical measurements
- **HIGHLY ORDERED CRYSTAL STRUCTURE**: more efficient charge transport

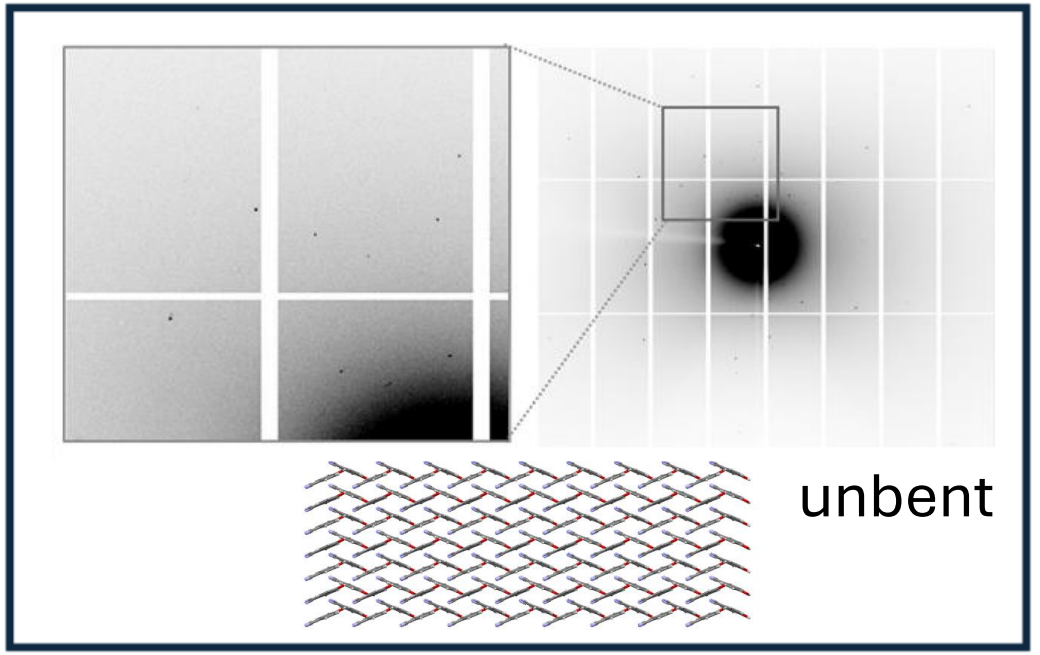
4HCB polymorphs

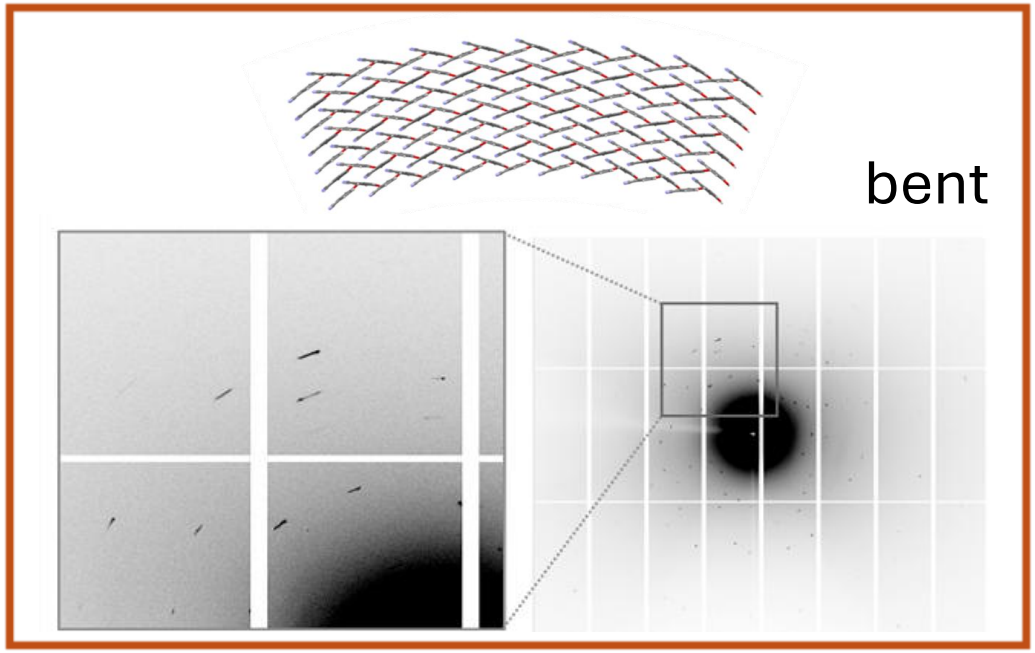






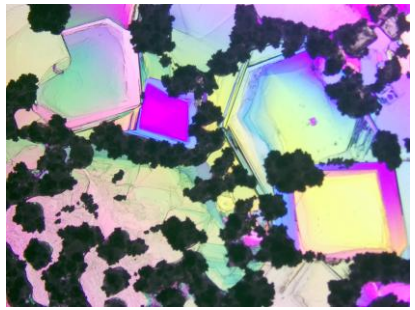
Crystal		α	β
m.p. (DSC)		113.8 °C	-
Space group		Pbcn centrosymmetric	$Pna2_1$ polar
Cell parameters	a	9.103(4) Å	7.395(1) Å
	b	10.570(3) Å	11.040(1) Å
	c	25.258(8) Å	7.537(1) Å
R-factor (%)		3.76	3.32





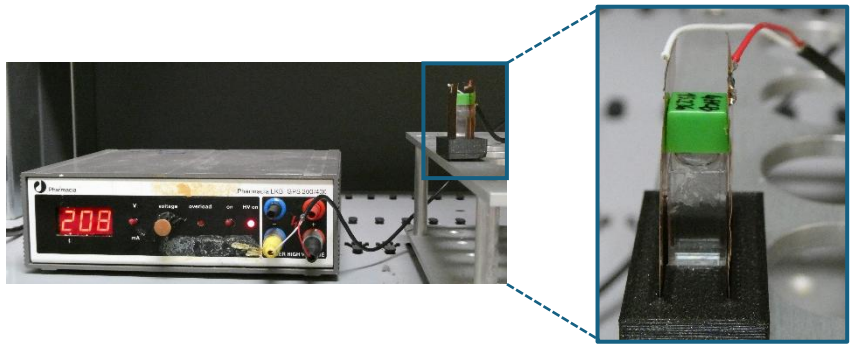
Searching for new polymorphs

- Various concentration, temperature, evaporation rate or solvent



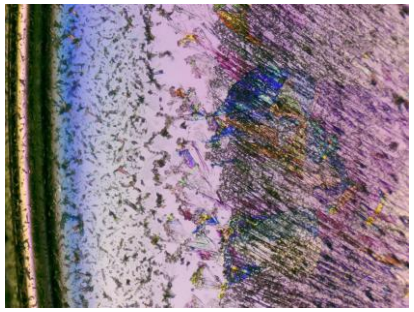
1-pentanol, lid closed
(0.67 X) Polarized light

- Solvent evaporation under electric field



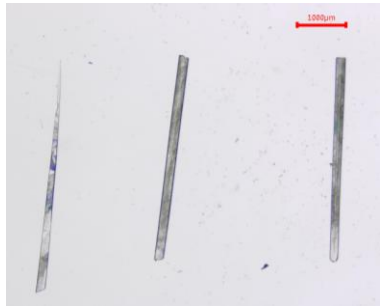
- Solvent evaporation under reduced pressure

Liophyzer (~0.2 mbar)



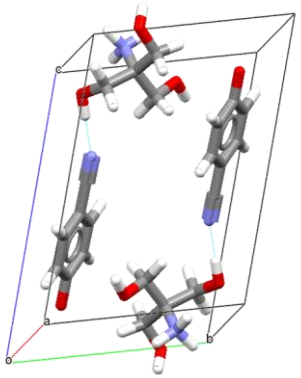
4HCB in 1-pentanol (80% saturation), plate ps, lid open, 0.2 mbar (2x)

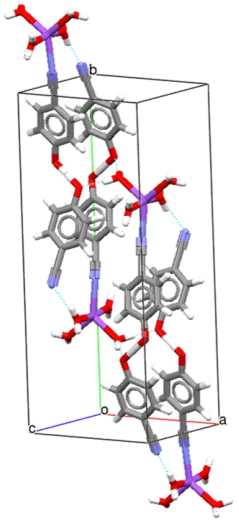
- Sublimation under reduced pressure (~2 mbar): new morphology of elongated rods

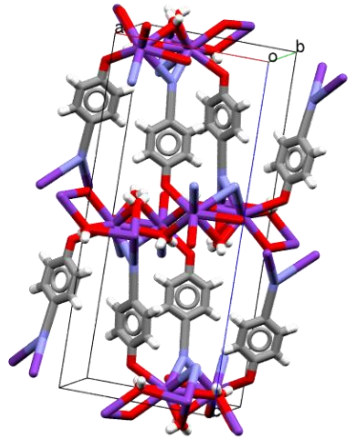


3 parts of a single 4HCB crystal from sublimation (5x)

4HCB derivatives



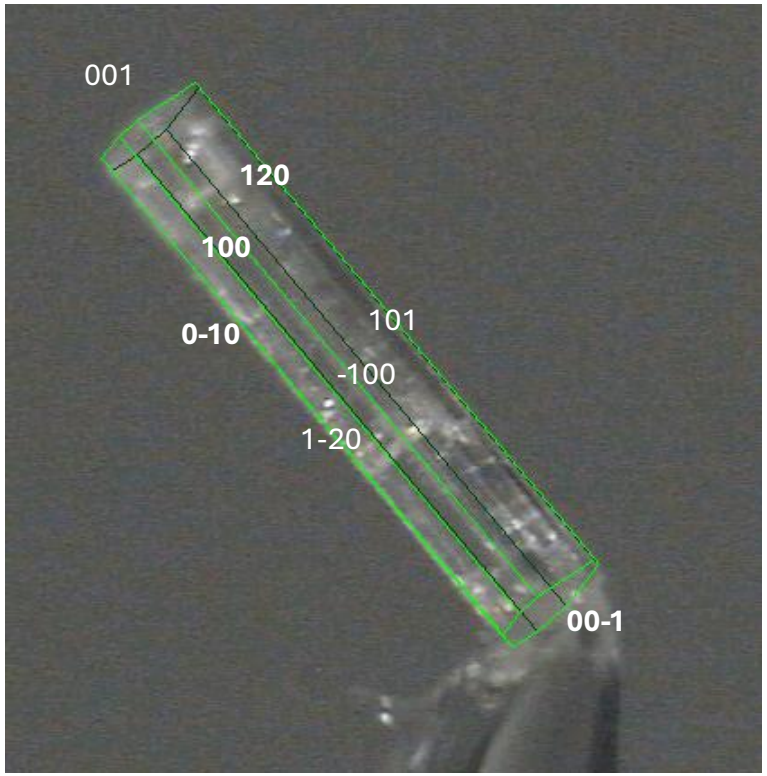




Crystal		$TRIS^{+}4HCB^{-}$	$4HCB/4HCB^{-}Na^{+}(H_2O)_4$	$4HCB^{-}K^{+}(H_2O)_2$
m.p. (DSC)		141 °C	97 °C	-
Space group		P-1 centrosymmetric	$P2_1/c$ centrosymmetric	P bca centrosymmetric
Cell parameters	a	5.686(1) Å	9.271(1) Å	10.371(8) Å
	b	8.794(1) Å	22.790(3) Å	7.230(3) Å
	c	12.335(1) Å	7.716(2) Å	23.440(16) Å
	α	73.01(1)	90	90
	β	77.52(1)	94.58(1)	90
	γ	89.19(1)	90	90
R-factor (%)		3.26	5.69	4.17

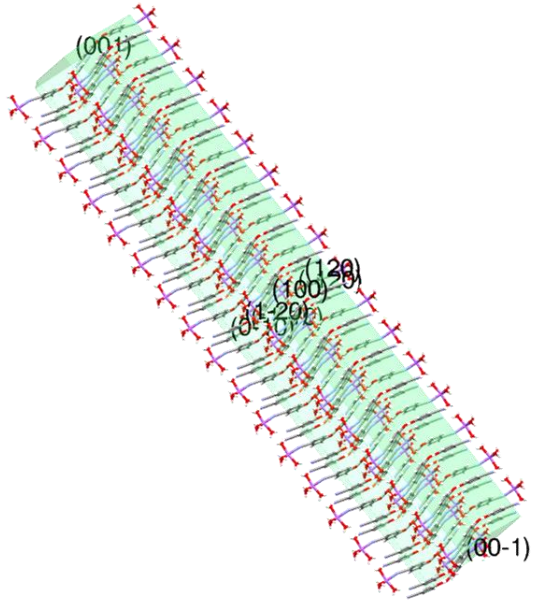
Crystals are anisotropic materials:
different crystal faces have different physical properties.

CRYSTAL ORIENTATION
and FACE INDEXING



4HCB/4HCB^{-}Na^{+}(H$_2$O)$_4$

CRYSTAL PACKING
ORIENTATION



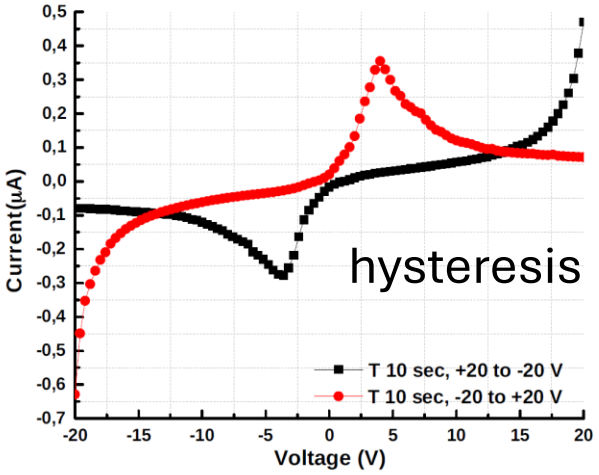
Also determinated for:

α-4HCB

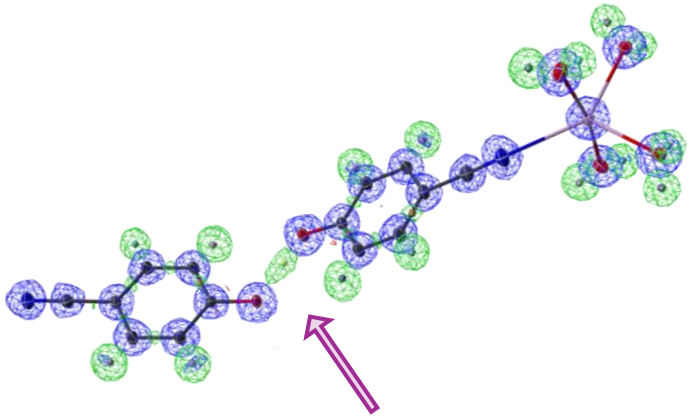
TRIS^{+}4HCB^{-}

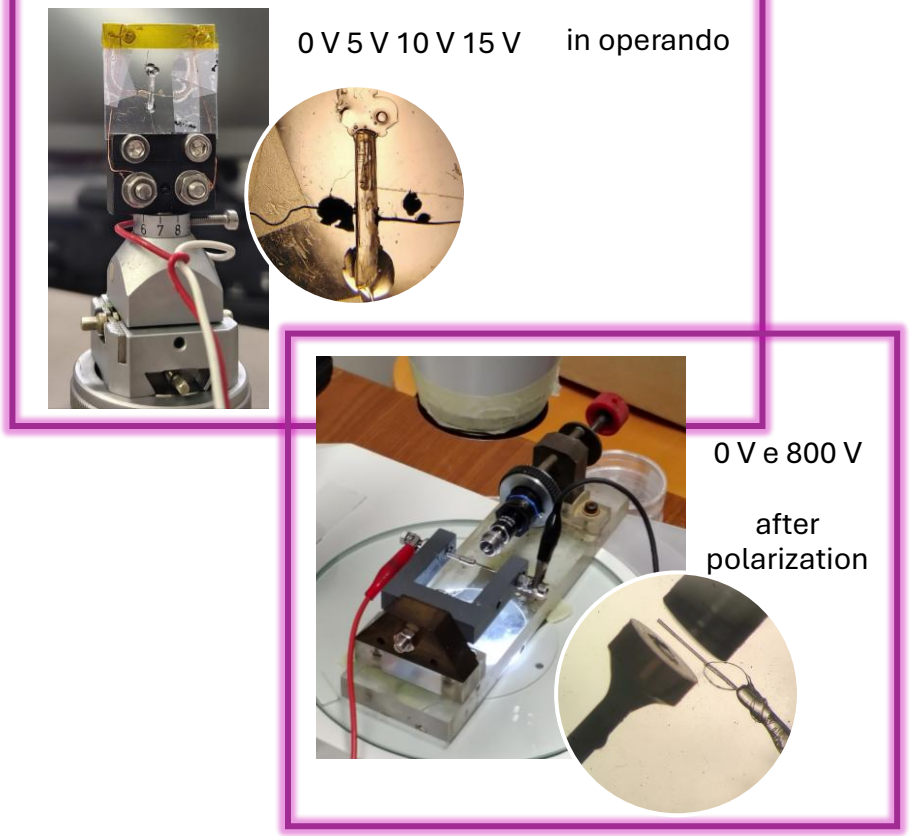
Electrical measurement

$4HCB/4HCB^{-}Na^{+}(H_2O)_4$
$TRIS^{+}4HCB^{-}$



$4HCB/4HCB^{-}Na^{+}(H_2O)_4$





Hypothesis: the application of a potential induces a polarization of the crystal.

This behaviour is typical of ferroelectric materials.

Observe the shift of the shared hydrogen atom (violet arrow)

Analyse this polarization effect using X-ray diffraction at the Elettra Synchrotron in Trieste (Italy). The polarization should correspond to the loss of centrosymmetry of the crystal.

Conclusions

- Several 4HCB polymorphs and derivative crystals were obtained and their structures were determined.
- Crystal orientation, face indexing and crystal packing analysis provide essential information for the interpretation of anisotropic electrical properties (the polarization).
- Electrical measurements on the $TRIS^{+}4HCB^{-}$ crystal and on the $4HCB/4HCB^{-}Na^{+}(H_2O)_4$ crystal revealed hysteresis curves, suggesting a possible polarization of the crystal. It requires further investigations.
- However, none of the investigated 4HCB derivatives crystallizes in a non-centrosymmetric space group and therefore no intrinsically polar crystal structure has been identified, so far.
- Further research is needed to identify new derivatives and polymorphs exhibiting the desired combination of flexibility and polarity properties.

Thank you for your kind attention

Acknowledgments

Prof. S. Geremia, Prof. N. J. Hickey, Dr. S. Joshi
University of Trieste (Italy)

Prof. A. Fraleoni-Morgera
University of G. D'Annunzio of Chieti-Pescara (Italy)

Dr. M. Polentarutti, Dr. G. Bais
XRD-1 beamline, Elettra Synchrotron Trieste (Italy)