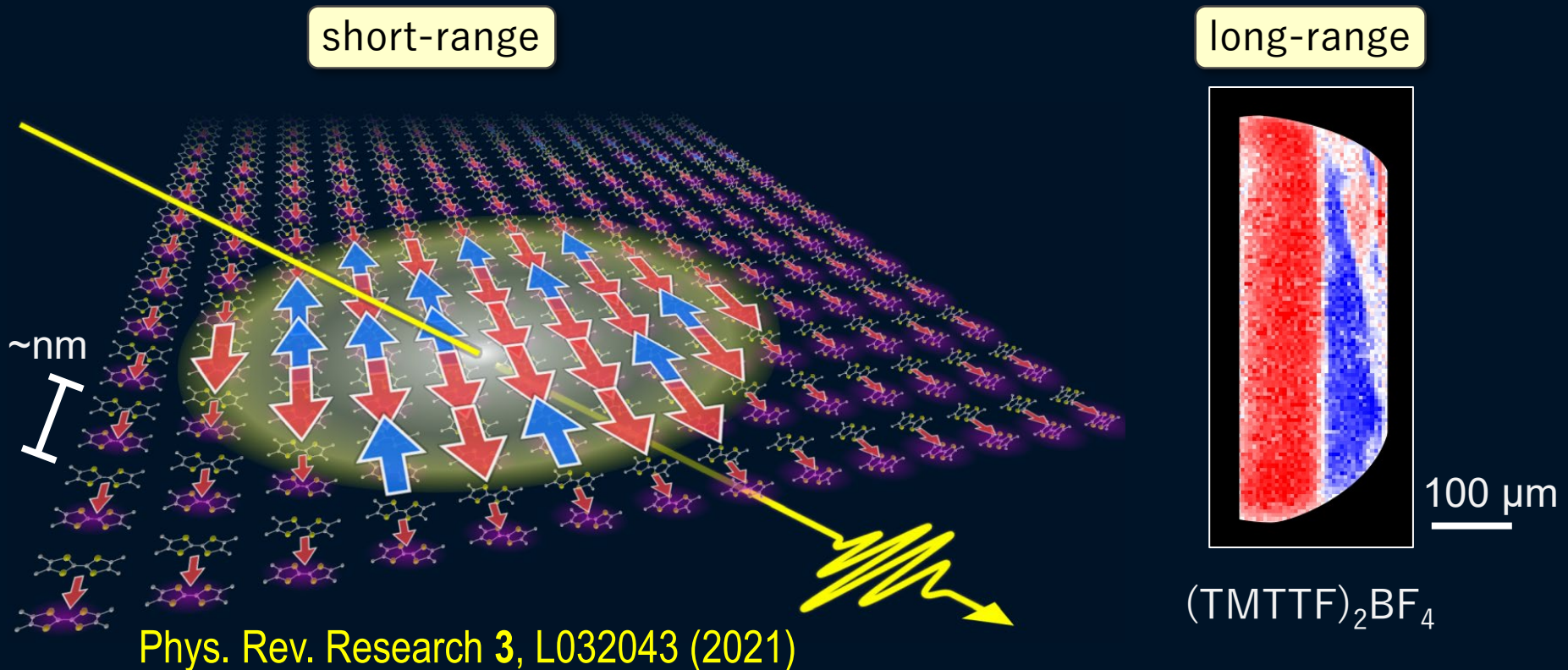


Short- and long-range charge correlations and their ultrafast photoinduced dynamics in organic electronic ferroelectrics

Hirotake Itoh (Tohoku Univ.)



collaborators



東北大学

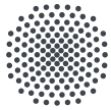
Tohoku University:

R. Minakami, H. Obatake, R. Fujiwara, T. Murakami, S. Sano, A. Kishida,
Y. Kawakami, S. Iwai



Okayama University of Science:

Kaoru Yamamoto



Universität
Stuttgart

Universität Stuttgart:

Martin Dressel



Tokyo Institute of Technology:

Y. Okimoto, S. Koshihara



Okayama University:

T. Fujiwara, N. Ikeda

supported by:

KAKENHI(18H01144, JP20H05147
("Quantum Liquid Crystal"), 22H01149)



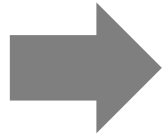
JST-CREST (JPMJCR1901)



MEXT Q-LEAP (JPMXS0118067426)

outline

terahertz experiments on $(\text{TMTTF})_2\text{X}$:
⇒ phase boundary is intriguing

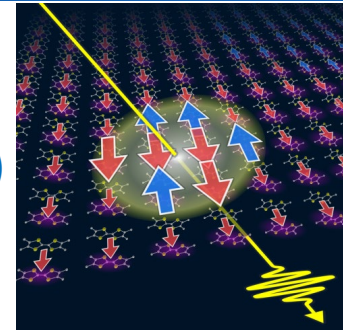


introduction (electronic ferroelectricity)

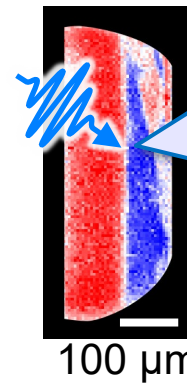
short- & long-range charge correlations

enhancement (0.1 ps)

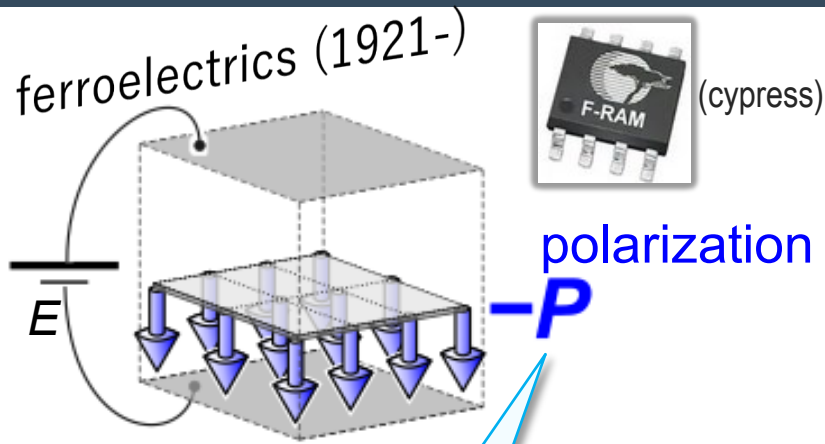
Itoh, Iwai *et al.*, Phys. Rev. Research 3, L032043 (2021)



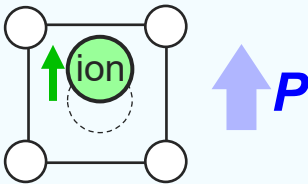
ferroelectric domains



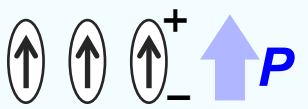
intense THz-excitation ($R\text{Fe}_2\text{O}_4$)



- displacive (ex. BaTiO_3)



- order-disorder (ex. Rochelle salt)



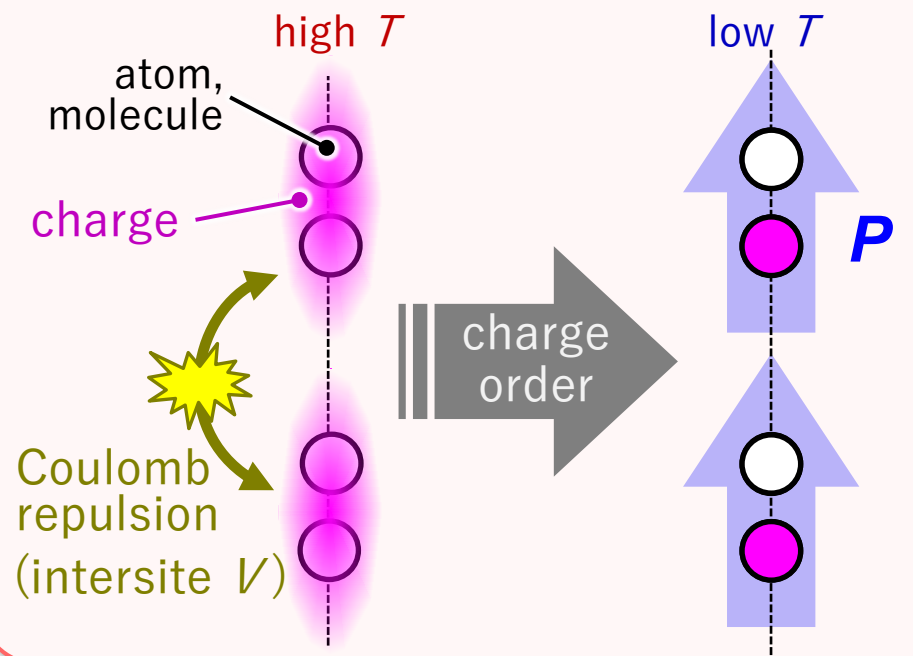
- magnetic (ex. TbMnO_3)

- **electronic**

(ex. $(\text{TMTTF})_2\text{X}$, $\alpha\text{-(ET)}_2\text{I}_3$, LuFe_2O_4)
Monceau *et al.*, Phys. Rev. Lett. (2001)

P by charge order (electronic crystal)

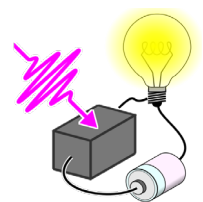
Brink *et al.*, J. Phys.: Condens. Matter (2008)
Ishihara, *ibid.* (2014); J. Phys. Soc. Jpn. (2010)



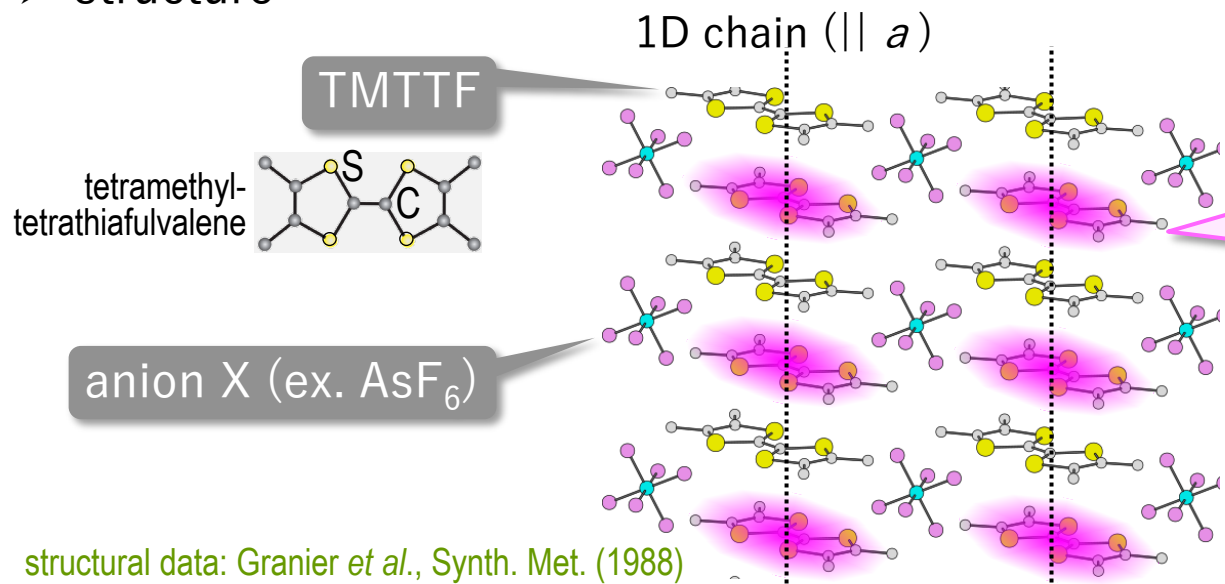
motivation:
lightweight electrons \rightarrow ultrafast photoresponse ?

ex. photoinduced phase transition

Koshihara *et al.*, Phys. Rep. (2021)
Basov *et al.*, Nature Mater. (2017)



➤ structure



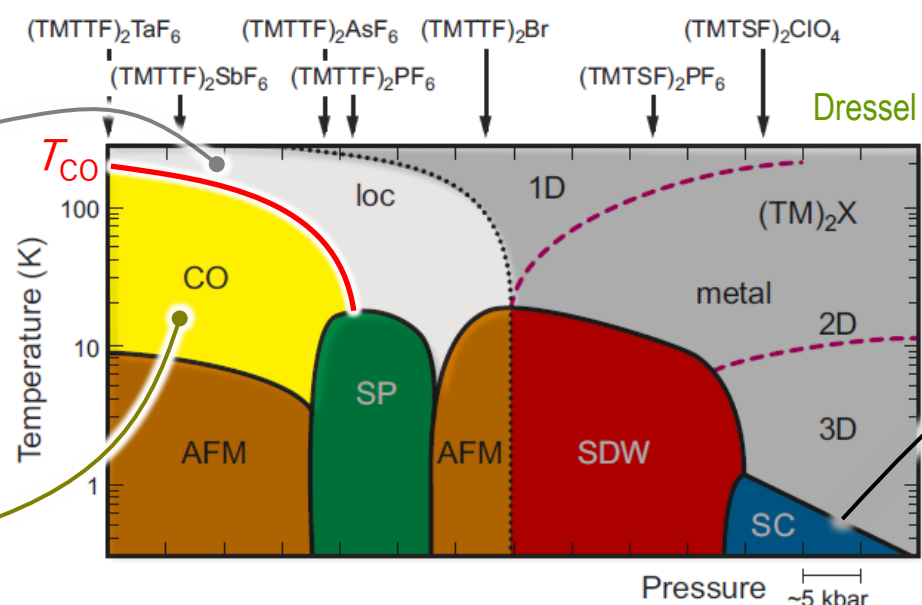
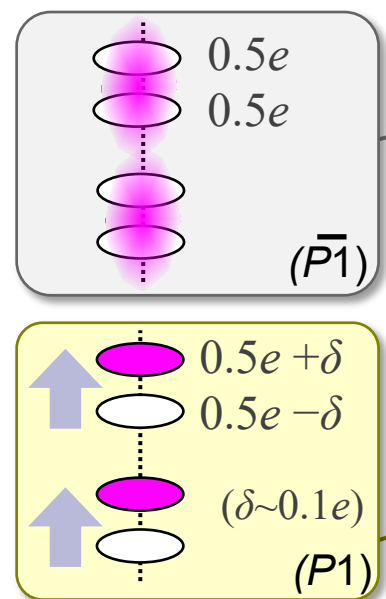
charge order (CO, $T < T_{CO}$)
(1/4 filling)

Chow *et al.*, Phys. Rev. Lett. (2000)
Seo *et al.*, J. Phys. Soc. Jpn. (1997)

⇒ electronic FE
Monceau *et al.*, Phys. Rev. Lett. (2001)

structural data: Granier *et al.*, Synth. Met. (1988)

➤ rich phases (correlated electron)



Dressel *et al.*, Crystals 2, 528 (2012)

Jérome *et al.*,
J. Physique Lett. 41, L95 (1980)

Phys. Rev. B **31**, 3583 (1985)

Structureless transition and strong localization effects in bis-tetramethyltetrathiafulvalenium salts [(TMTTF)₂X]

C. Coulon and S. S. P. Parkin

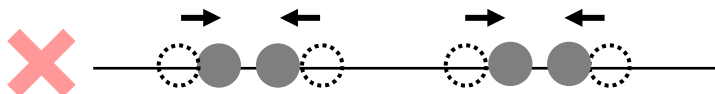
IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193

R. Laversanne

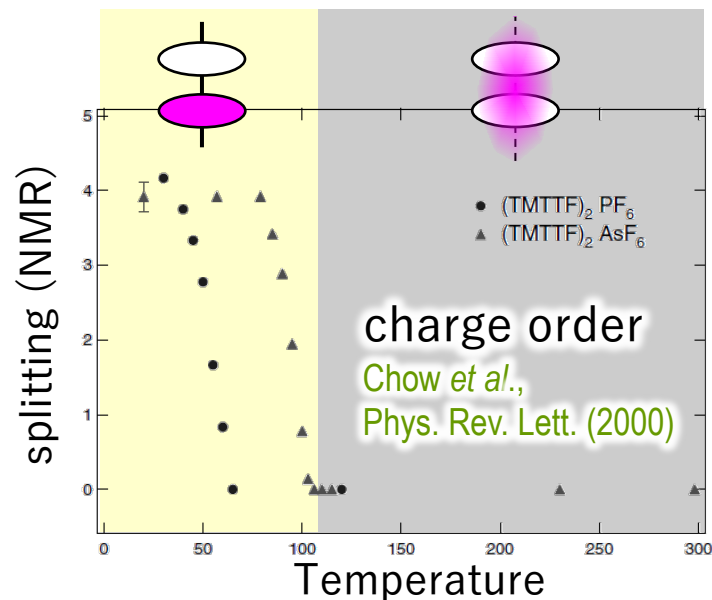
Centre de Recherches Paul Pascal, Domaine Universitaire, F-33405 Talence Cédex, France

(Received 28 September 1984)

unlike Peierls transition



cf. Kitou *et al.*, PRL (2017)



electronic FE (dielectric experiments)

Monceau *et al.*, PRL **86**, 4080 (2001)

VOLUME 86, NUMBER 18 PHYSICAL REVIEW LETTERS 30 APRIL 2001

Ferroelectric Mott-Hubbard Phase of Organic (TMTTF)₂X Conductors

P. Monceau,¹ F. Ya. Nad,^{1,2} and S. Brazovskii^{3,4}

¹Centre de Recherches sur les Très Basses Températures, laboratoire associé à l'Université Joseph Fourier, CNRS, BP 166, 38042 Grenoble cedex 9, France

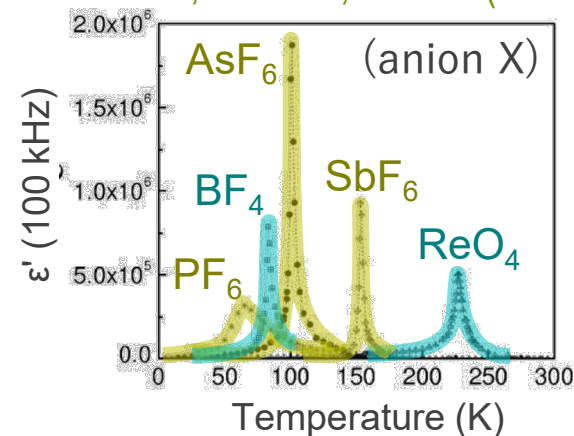
²Institute of Radio-Engineering and Electronics, 103907 Moscow, Russia

³Laboratoire de Physique Théorique et des Modèles Statistiques, CNRS, Bâtiment 100, Université Paris-Sud, 91405 Orsay cedex, France

⁴L. D. Landau Institute for Theoretical Physics, Moscow, Russia

(Received 13 December 2000)

Nad *et al.*, JPSJ **75**, 051005 (2006)



ESR, Raman, ...

Coulon *et al.*, Eur. Phys. J. B **88**, 85 (2015)

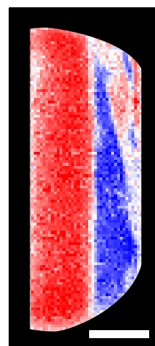
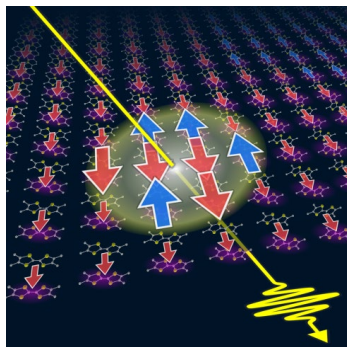
Yasin *et al.*, Phys. Rev. B **85**, 144428 (2012)

Świetlik *et al.*, Phys. Rev. B **95**, 085205 (2017)

our approach:
ultrafast terahertz (THz) spectroscopy

$(\text{TMTTF})_2\text{X}$

(this talk)



100 μm

$\alpha\text{-(ET)}_2\text{I}_3$

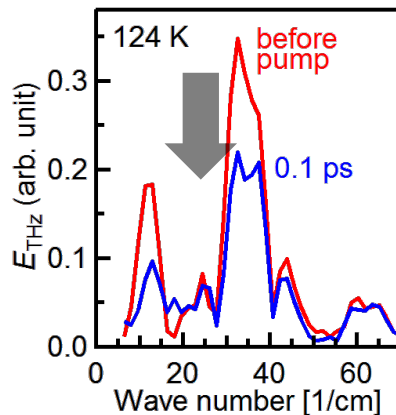
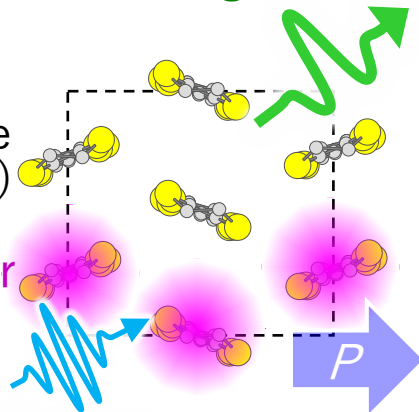
THz generation

ultrafast ($\sim 0.1 \text{ ps} = 10^{-13} \text{ s}$) metal transition

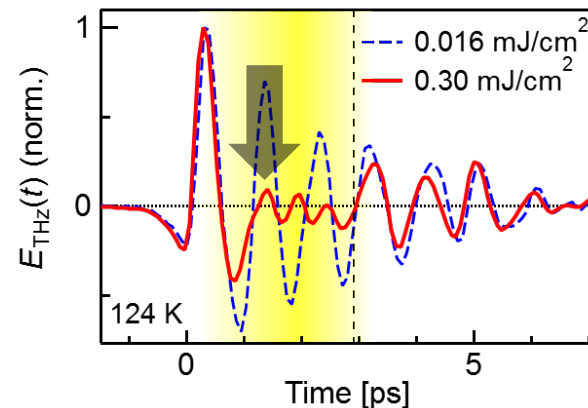
ET molecule
(BEDT-TTF)

charge order

photoexcitation

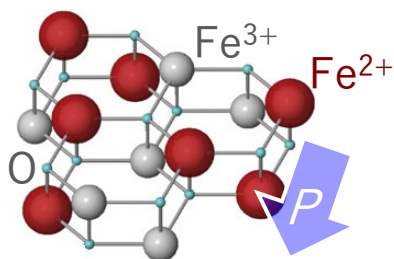


Hi, Iwai *et al.*,
Appl. Phys. Lett. **104**, 173302 (2014)



Hi, Iwai *et al.*,
Appl. Phys. Lett. **112**, 093302 (2018)

LuFe_2O_4



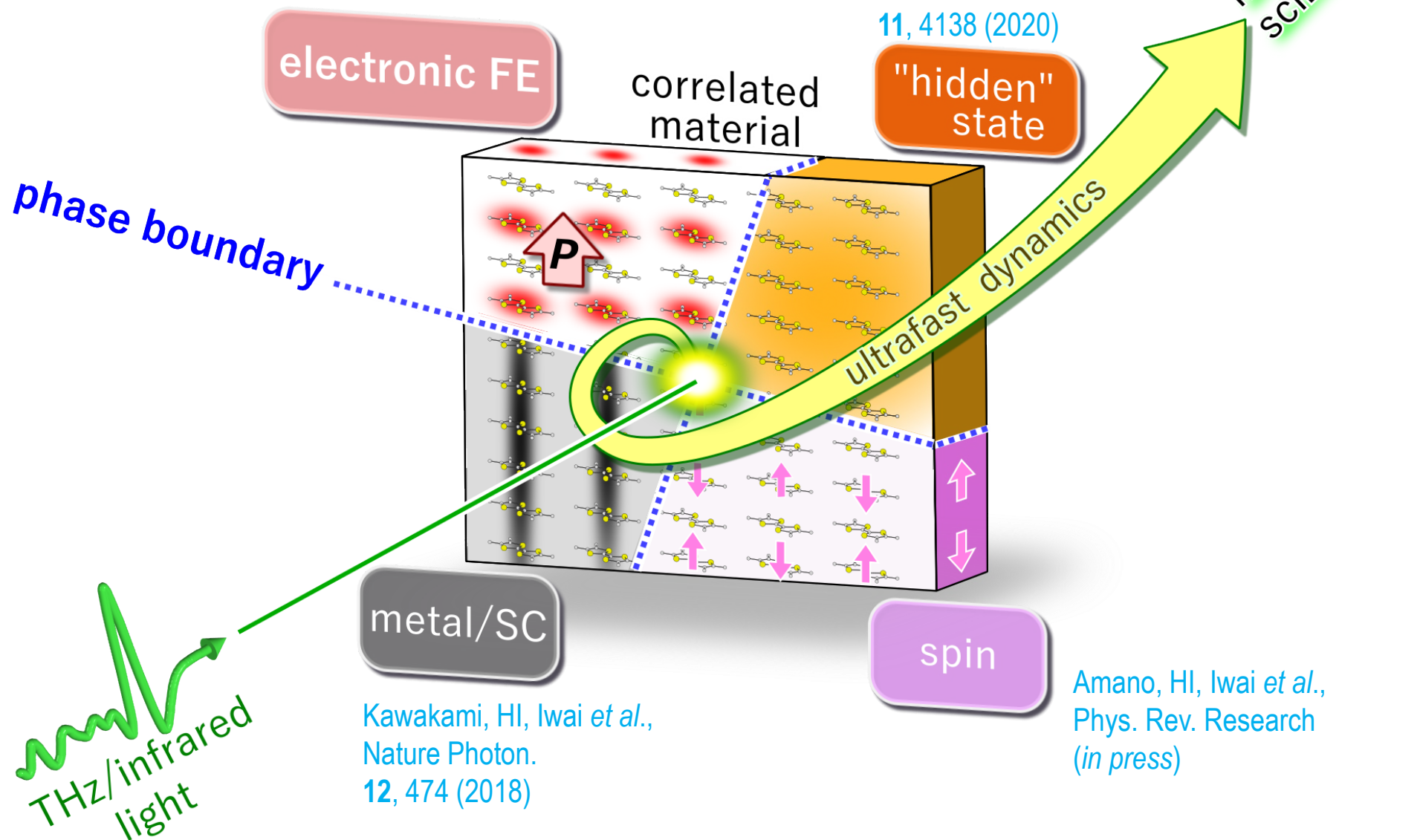
photoinduced CO melting
 P steering (intense THz)

Hi, Iwai *et al.*,
J. Lumin. **133**, 149 (2013)

HI, Iwai *et al.*,
Phys. Rev. Research **3**, L032043 (2021)
Appl. Phys. Lett. **112**, 093302 (2018); **104**, 173302 (2014)

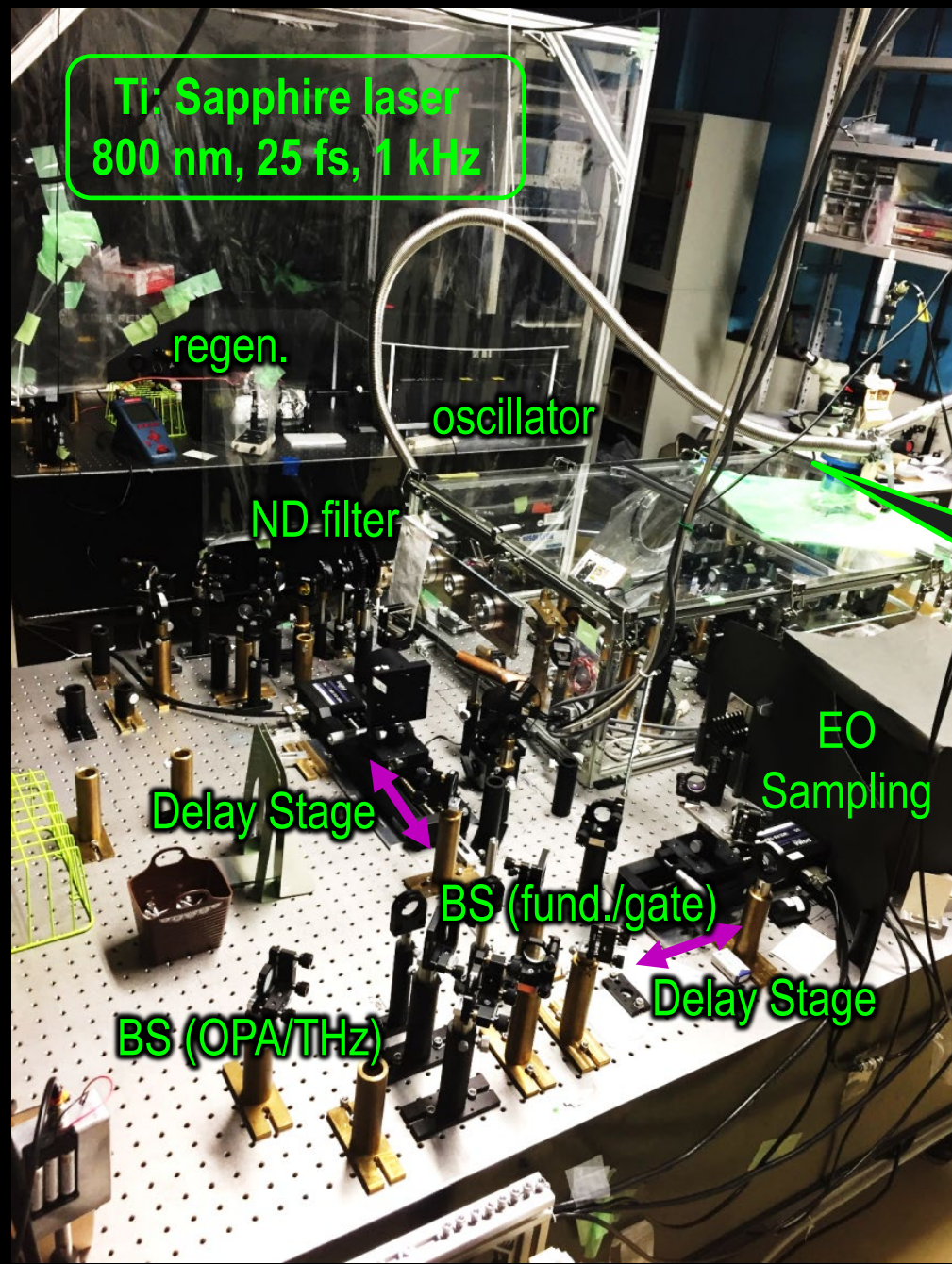
Kawakami, HI, Iwai *et al.*,
Nature Commun. **11**, 4138 (2020)

novel
sci. & tech.



Kawakami, HI, Iwai *et al.*,
Nature Photon. **12**, 474 (2018)

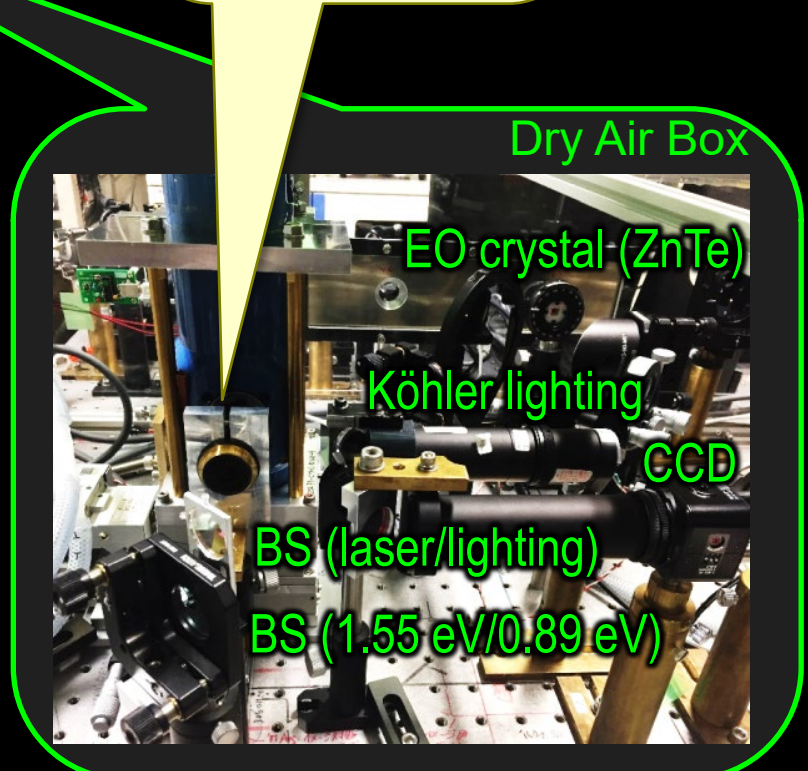
Amano, HI, Iwai *et al.*,
Phys. Rev. Research
(in press)



(TMTTF)₂X single crystal



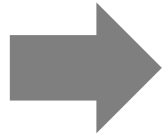
X = AsF₆
(*ab* plane)



outline

terahertz experiments on $(\text{TMTTF})_2\text{X}$:
⇒ phase boundary is intriguing

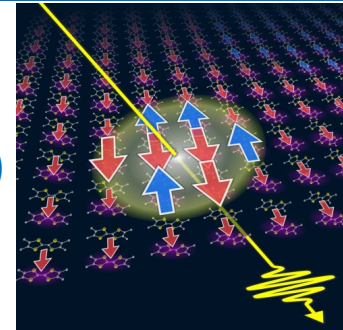
introduction (electronic ferroelectricity)



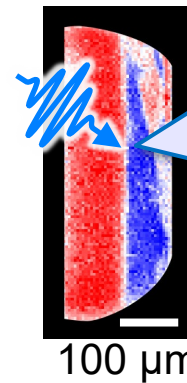
short- & long-range charge correlations

enhancement (0.1 ps)

Itoh, Iwai *et al.*, *Phys. Rev. Research* **3**, L032043 (2021)



ferroelectric domains

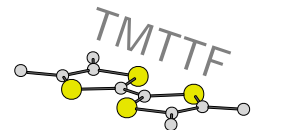


intense THz-excitation ($R\text{Fe}_2\text{O}_4$)

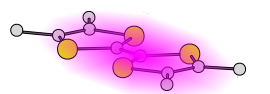
- ✓ ultrafast dynamics
- ✓ non-contact (cf. $\rho_a(\text{DC}) \sim 10 \Omega\text{cm}$)

cf. $\alpha\text{-(ET)}_2\text{I}_3$ Nakaya *et al.*, Phys. Rev. B **81**, 155111 (2010)
Itoh *et al.*, Appl. Phys. Lett. **112**, 093302 (2018);
ibid. **104**, 173302 (2014)

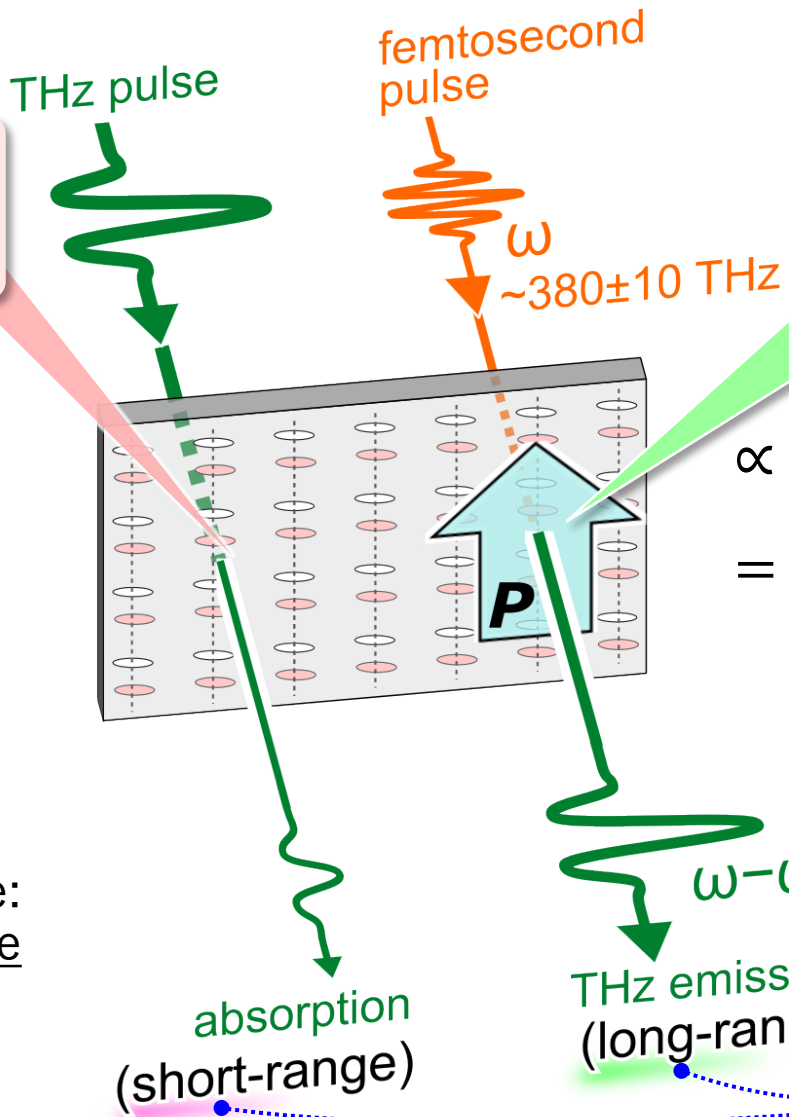
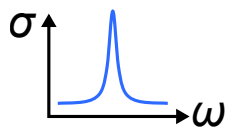
Tc mode ($\sim 65 \text{ cm}^{-1}$)
(intermolecular vibration)
Dressel et al., Crystals (2012)



IR inactive



w/ charge imbalance:
active

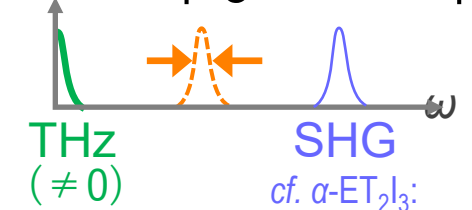


nonlinear process (2nd) by P
(centrosymmetry breaking)

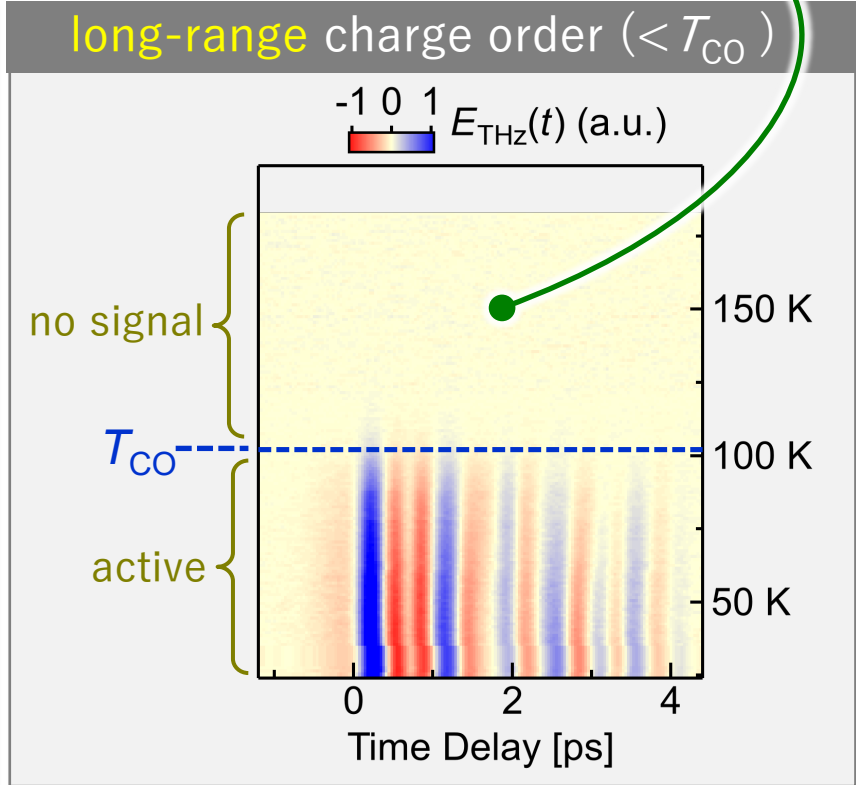
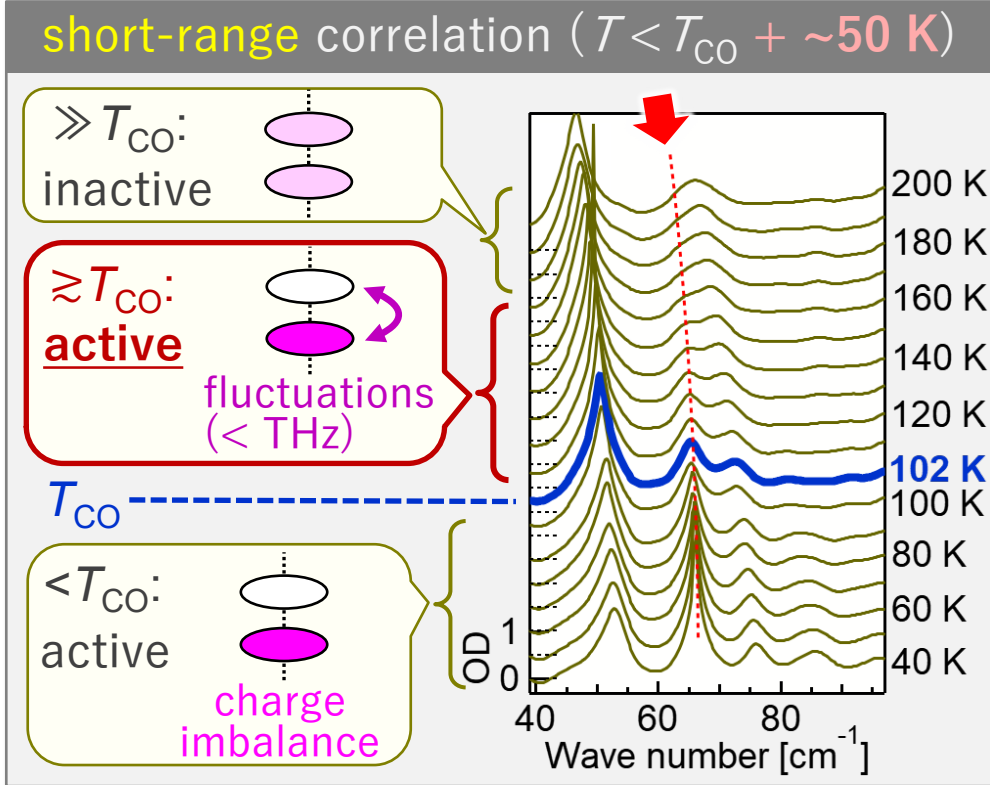
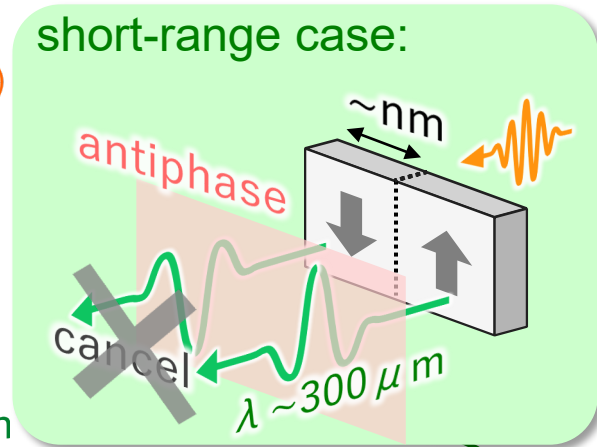
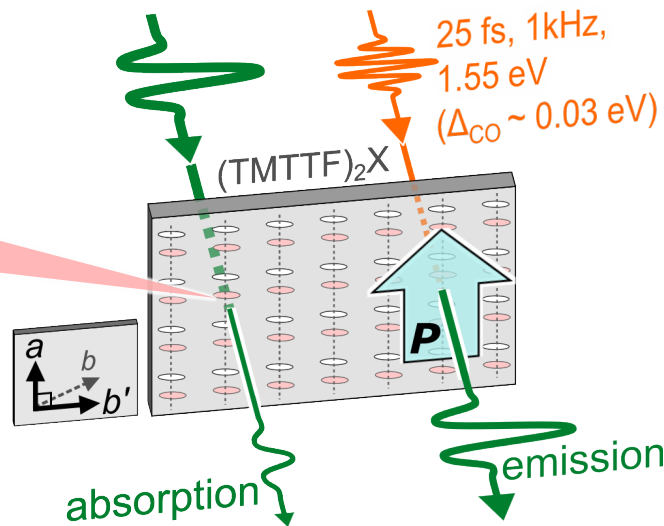
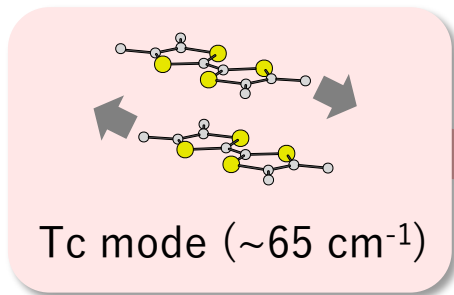
$$P_{\text{NL}}^{(2)} = \chi^{(2)} EE$$

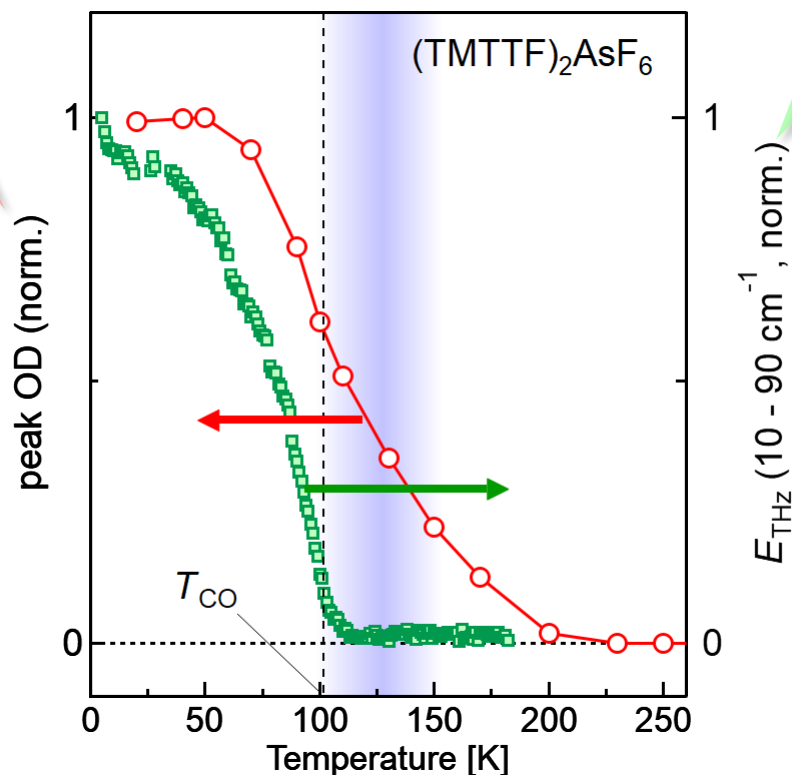
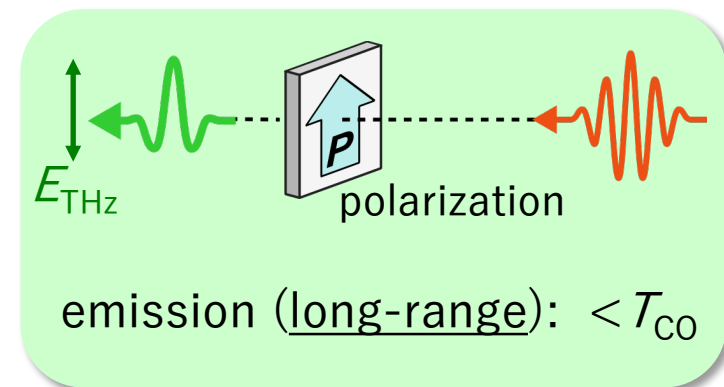
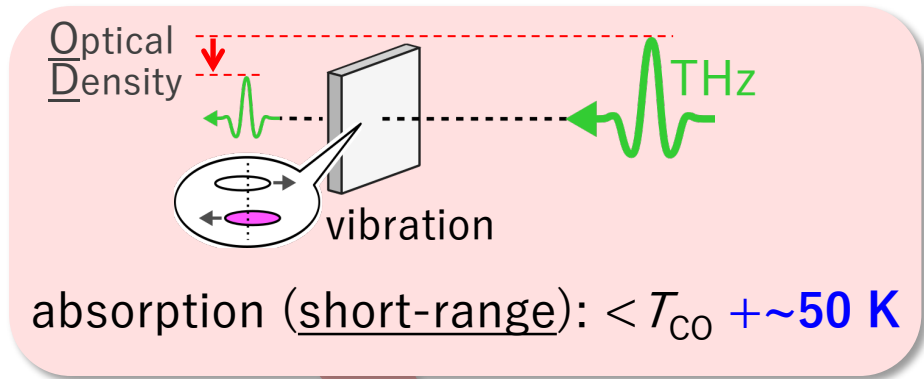
$$\propto [e^{i\omega t} + \text{c.c.}]^2$$

$$= e^{i(\omega - \omega)t} + e^{i(\omega + \omega)t} + \text{c.c.}$$



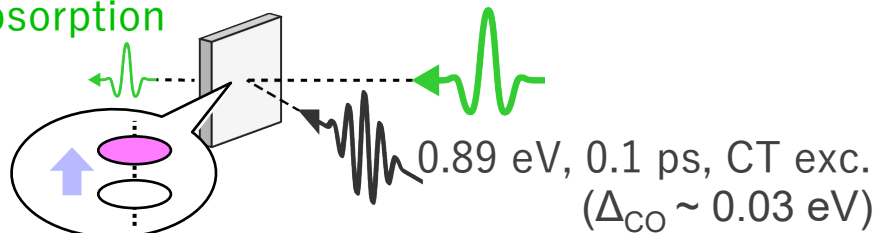
cf. $\alpha\text{-ET}_2\text{I}_3$:
Yamamoto, Iwai *et al.*,
JPSJ ('08), ICSM ('12)



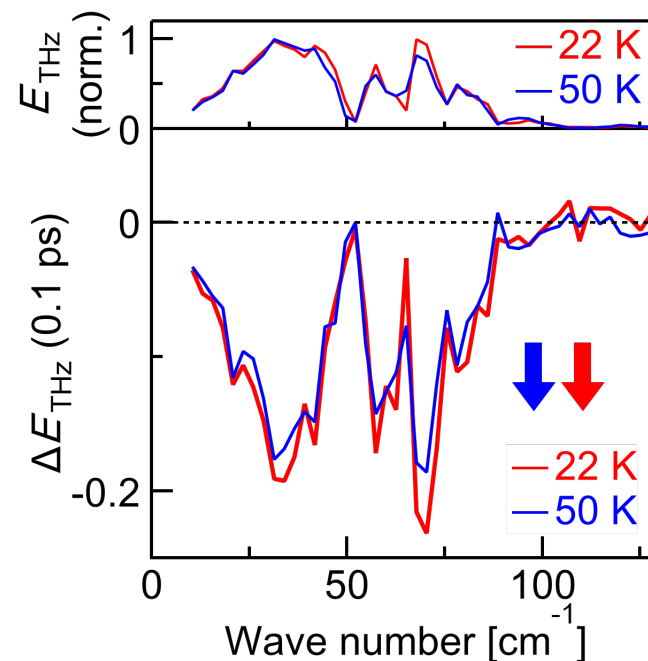
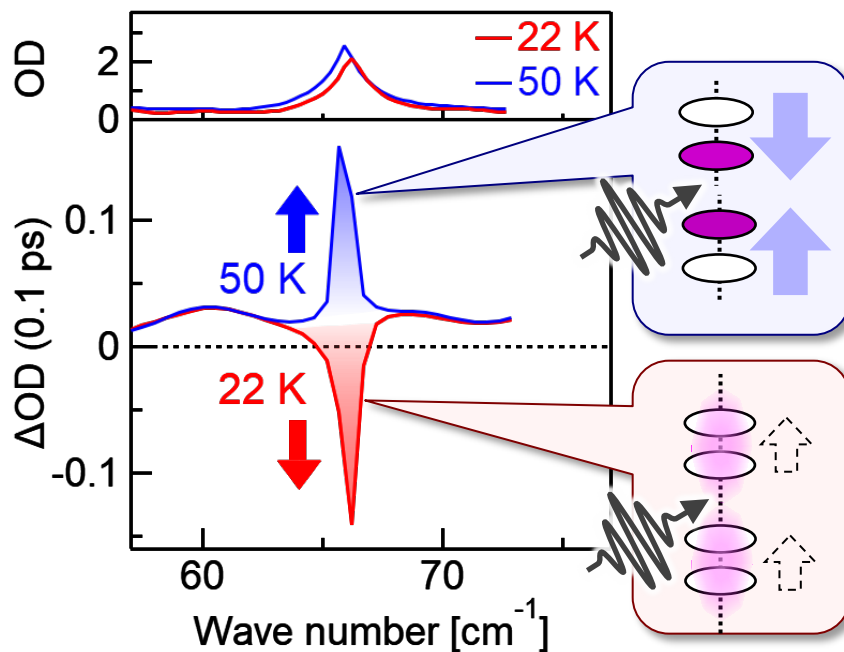
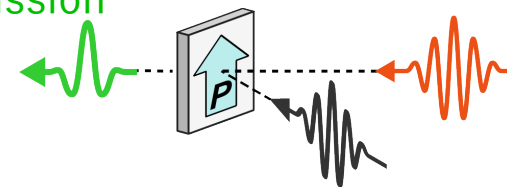


disentangle short- & long-range charge correlations
→ photoinduced dynamics ?

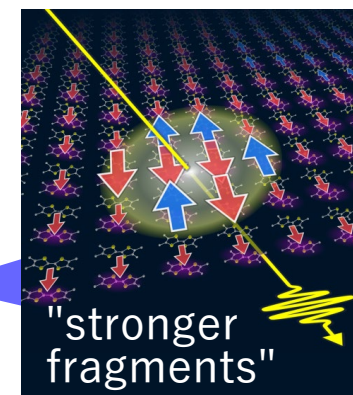
absorption



emission



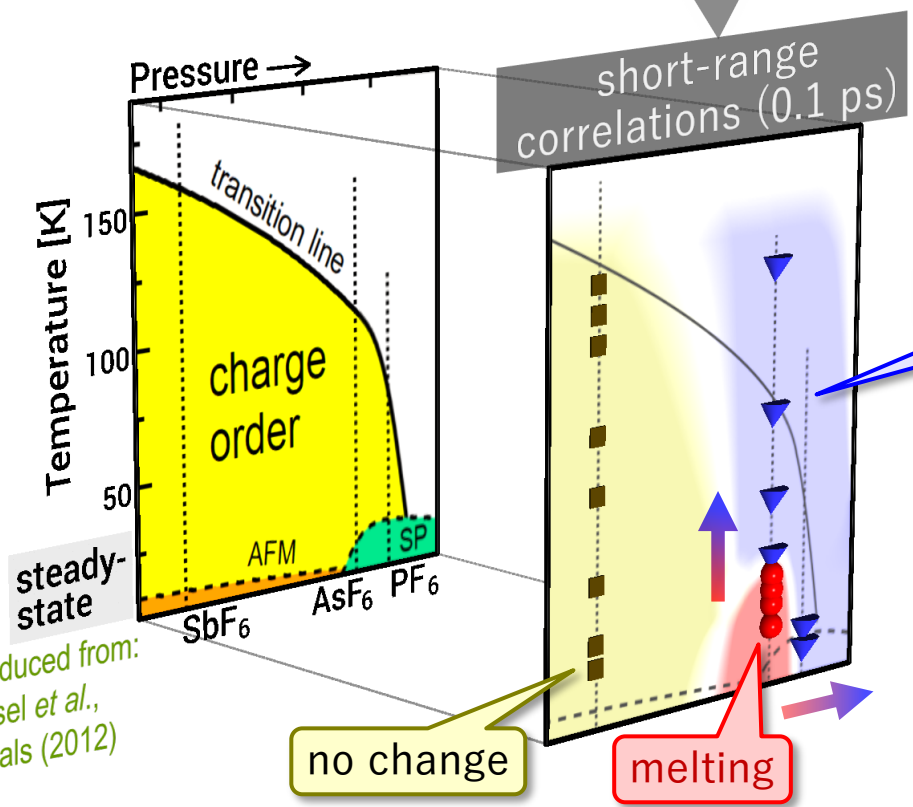
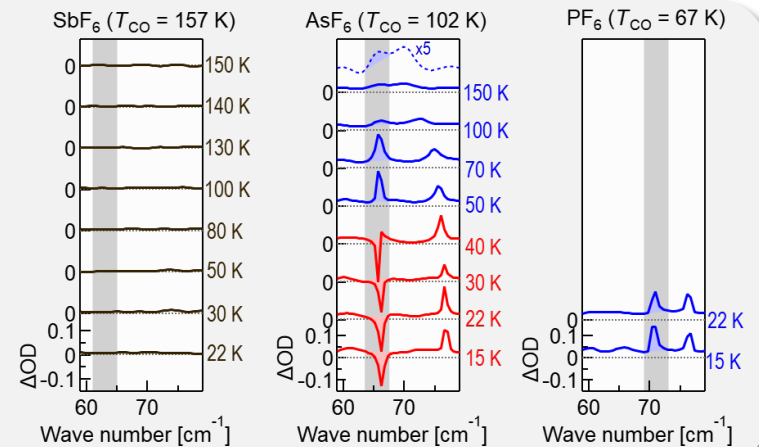
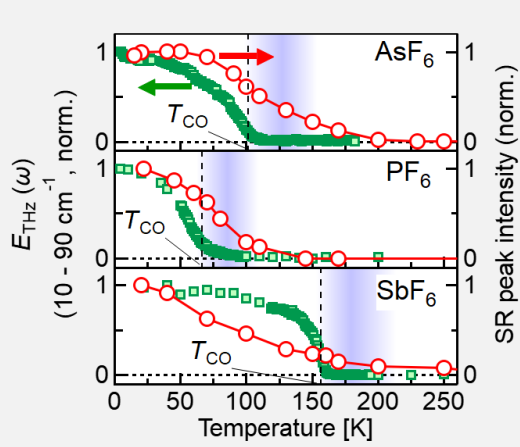
	short-range (ΔOD)	long-range (ΔE_{THz})
22 K	↓ (charge-order melting)	↓
50 K	↑ (enhancement)	↓ (∴ disorder)



anion substitution
($X = \text{SbF}_6, \text{AsF}_6, \text{PF}_6$)



chemical pressure



enhancement @ phase boundary
(charge fluctuations)

design strategy for
photoinduced phase transitions

outline

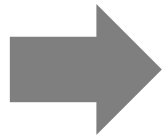
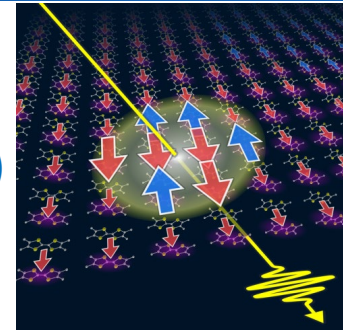
terahertz experiments on $(\text{TMTTF})_2\text{X}$:
⇒ phase boundary is intriguing

introduction (electronic ferroelectricity)

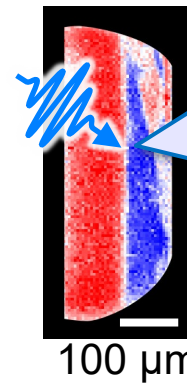
short- & long-range charge correlations

enhancement (0.1 ps)

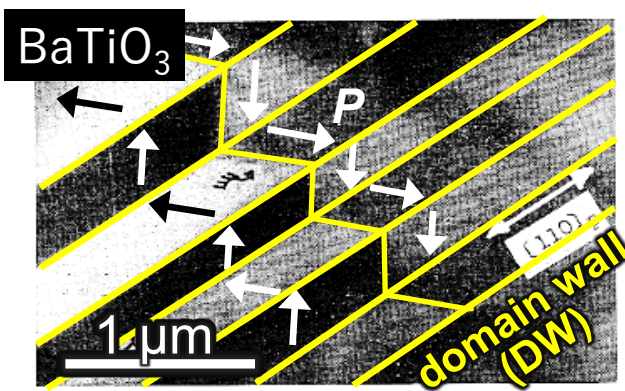
Itoh, Iwai *et al.*, *Phys. Rev. Research* **3**, L032043 (2021)



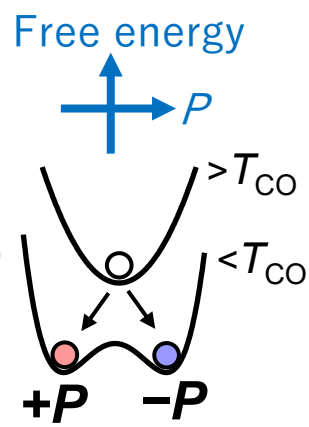
ferroelectric domains



intense THz-excitation ($R\text{Fe}_2\text{O}_4$)



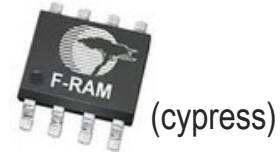
Tanaka *et al.*, JPSJ 19, 954 (1964)



"macroscopic regions of self-organized P "

- physics
Meier *et al.*, J. Appl. Phys. (2021) (special issue)

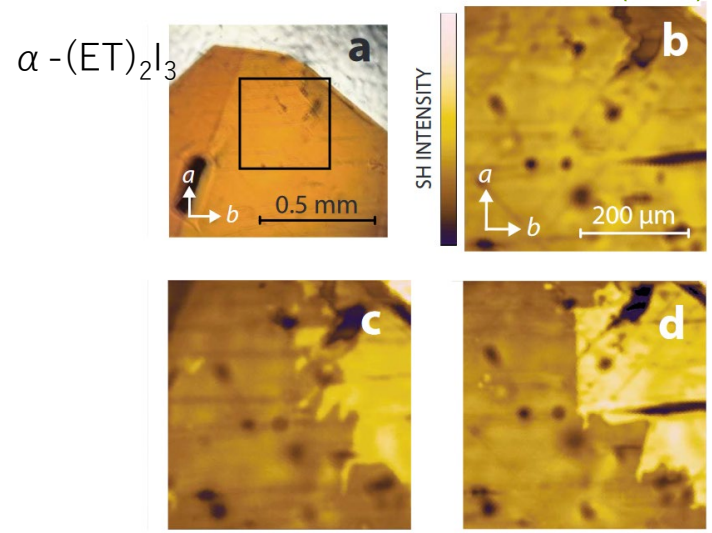
- application (memory)



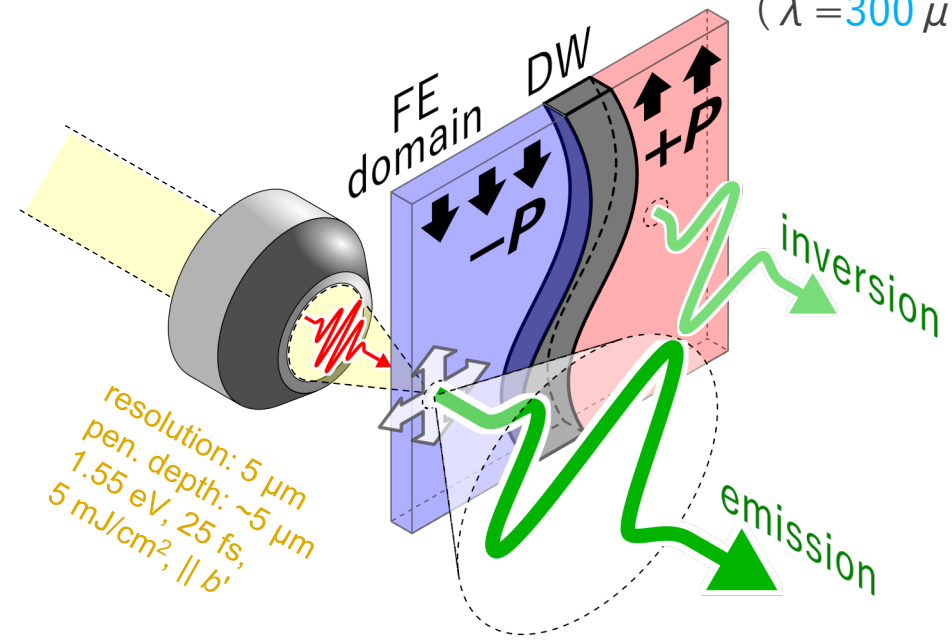
How to visualize antiparallel ($\pm P$) e-FE domains ?

SHG($\omega + \omega$)
hard ! (interference @ $\lambda = 0.4 \mu m$)

Yamamoto *et al.*, APL 96, 122901 (2010)

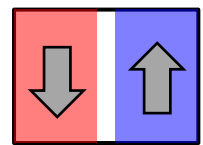
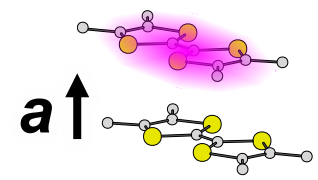
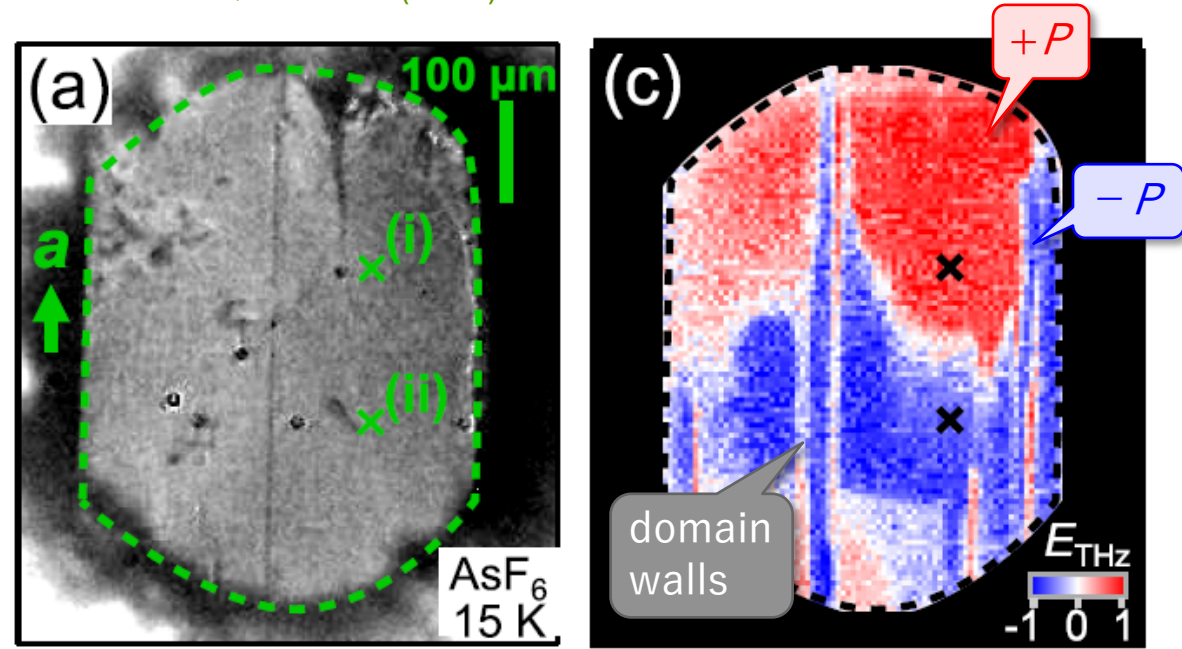


this work: THz emission ($\omega - \omega$) microscopy
($\lambda = 300 \mu m$)



cf. croconic acid Sotome *et al.*, Appl. Phys. Lett. (2014)

Hi, Iwai *et al.*, Phys. Rev. Research **3**, L032043 (2021)



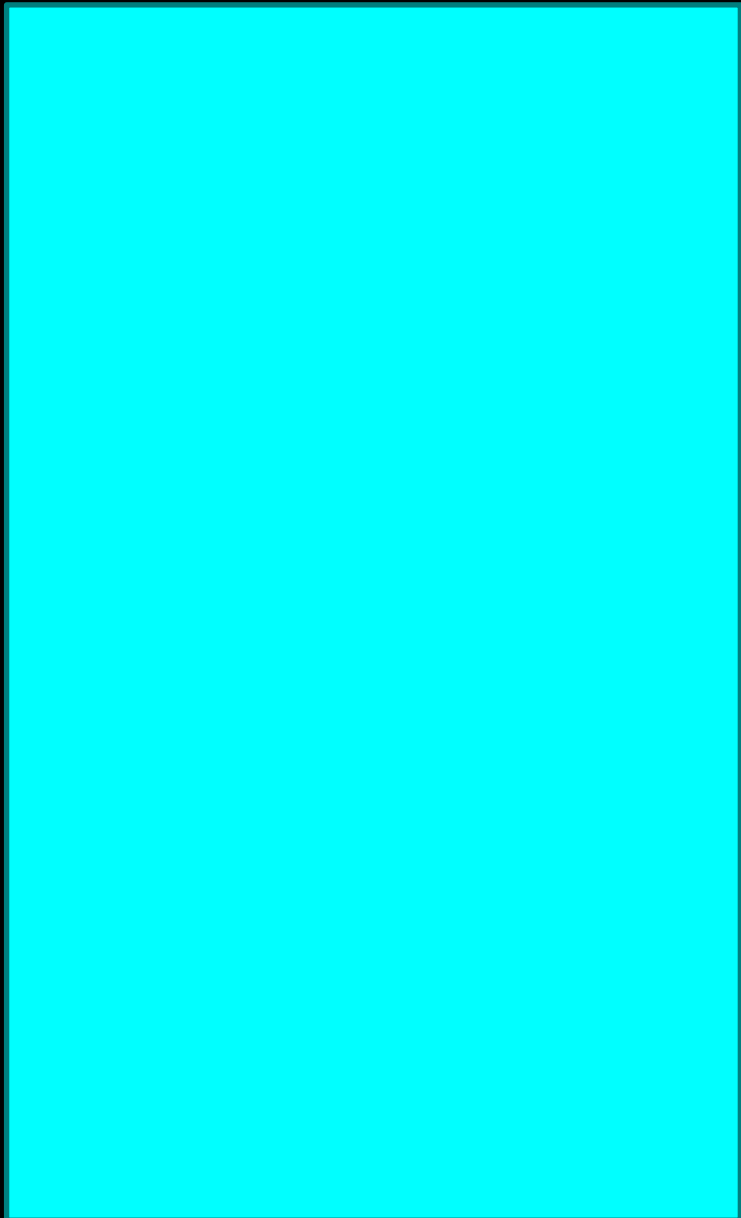
$\mathbf{P} \parallel \text{DW}$
 $\Rightarrow \text{div } \mathbf{P} = 0$
 (favorable)

- $\sim 100 \mu\text{m}$ characteristic size
- domain walls $\parallel a$: reasonable for " $\mathbf{P} \parallel a$ "

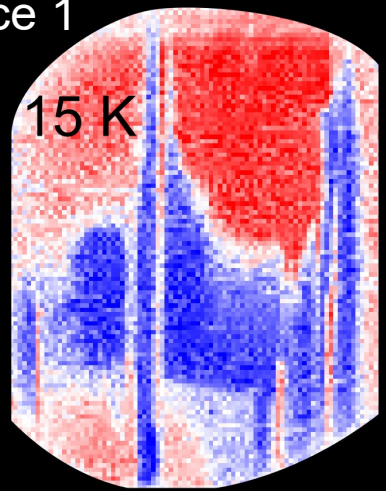
$X = \text{SbF}_6$

$X = \text{AsF}_6$

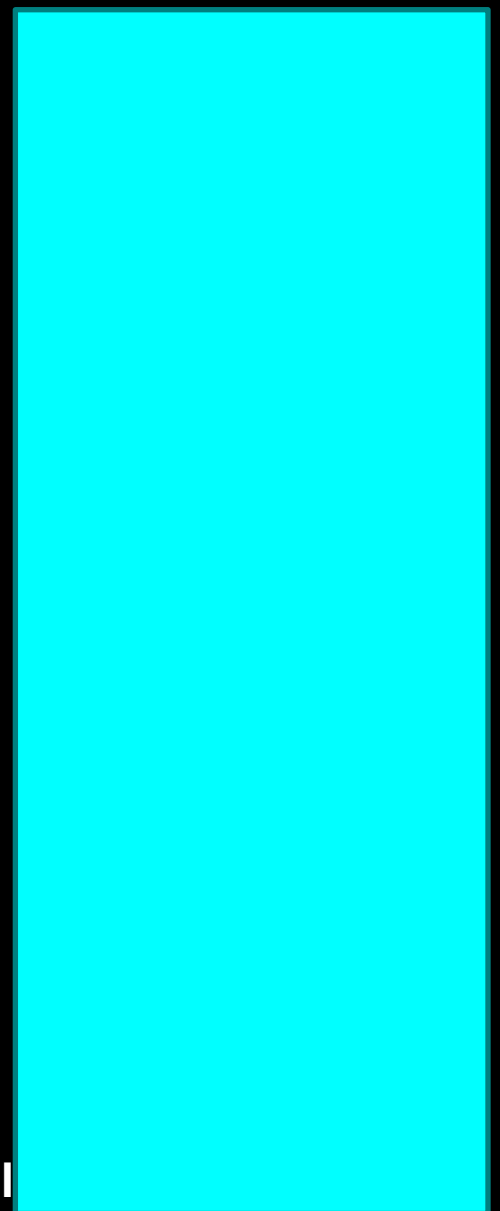
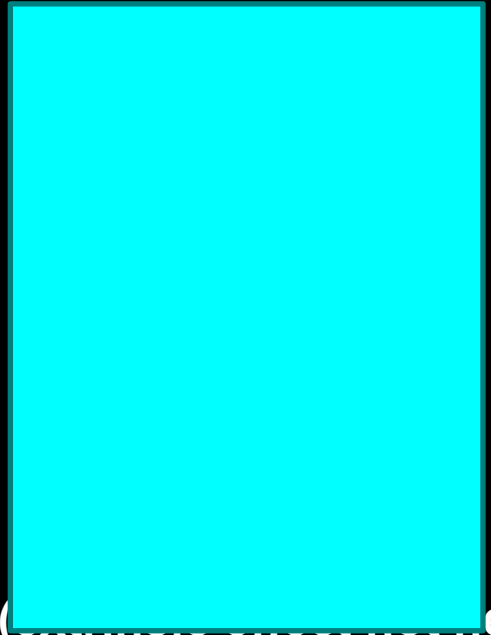
$X = \text{PF}_6$



piece 1



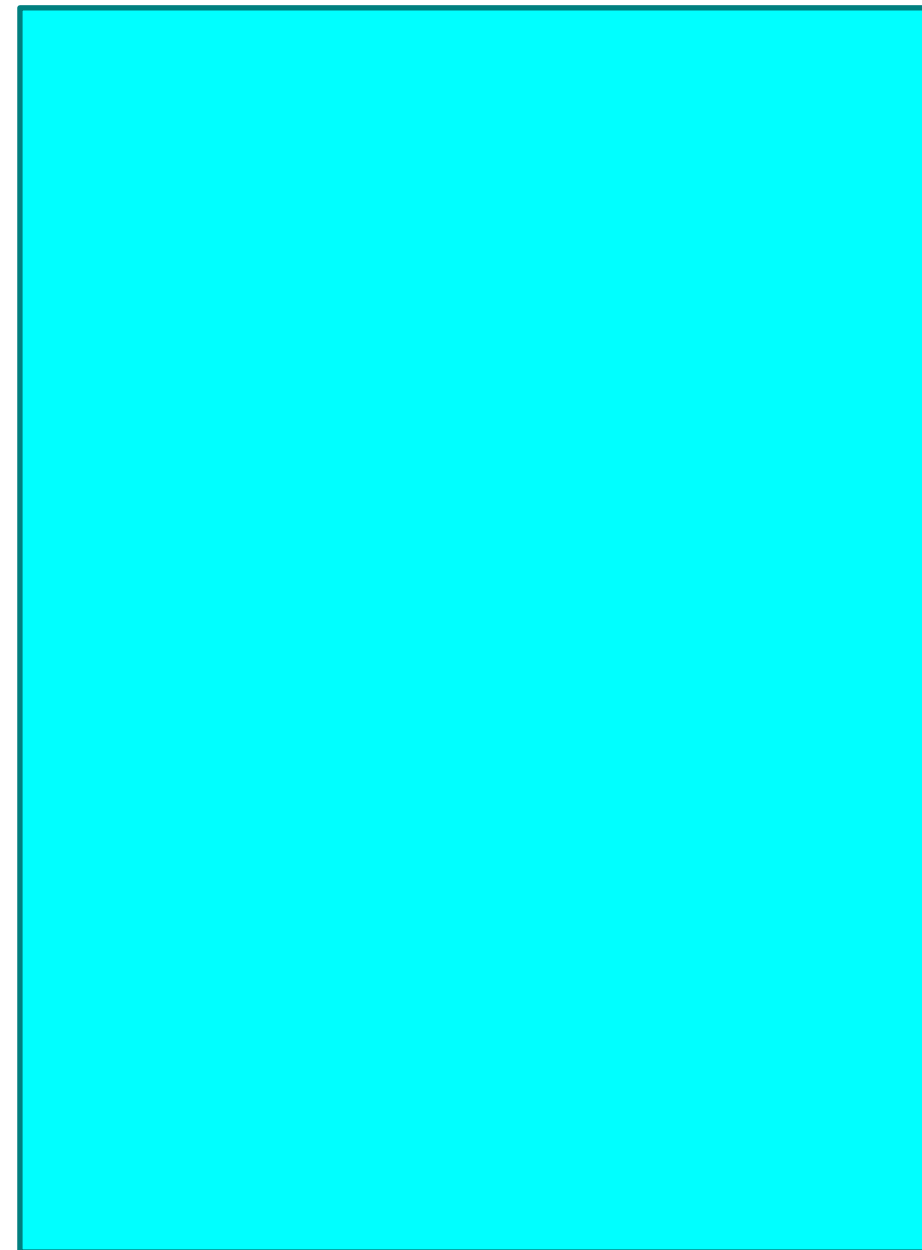
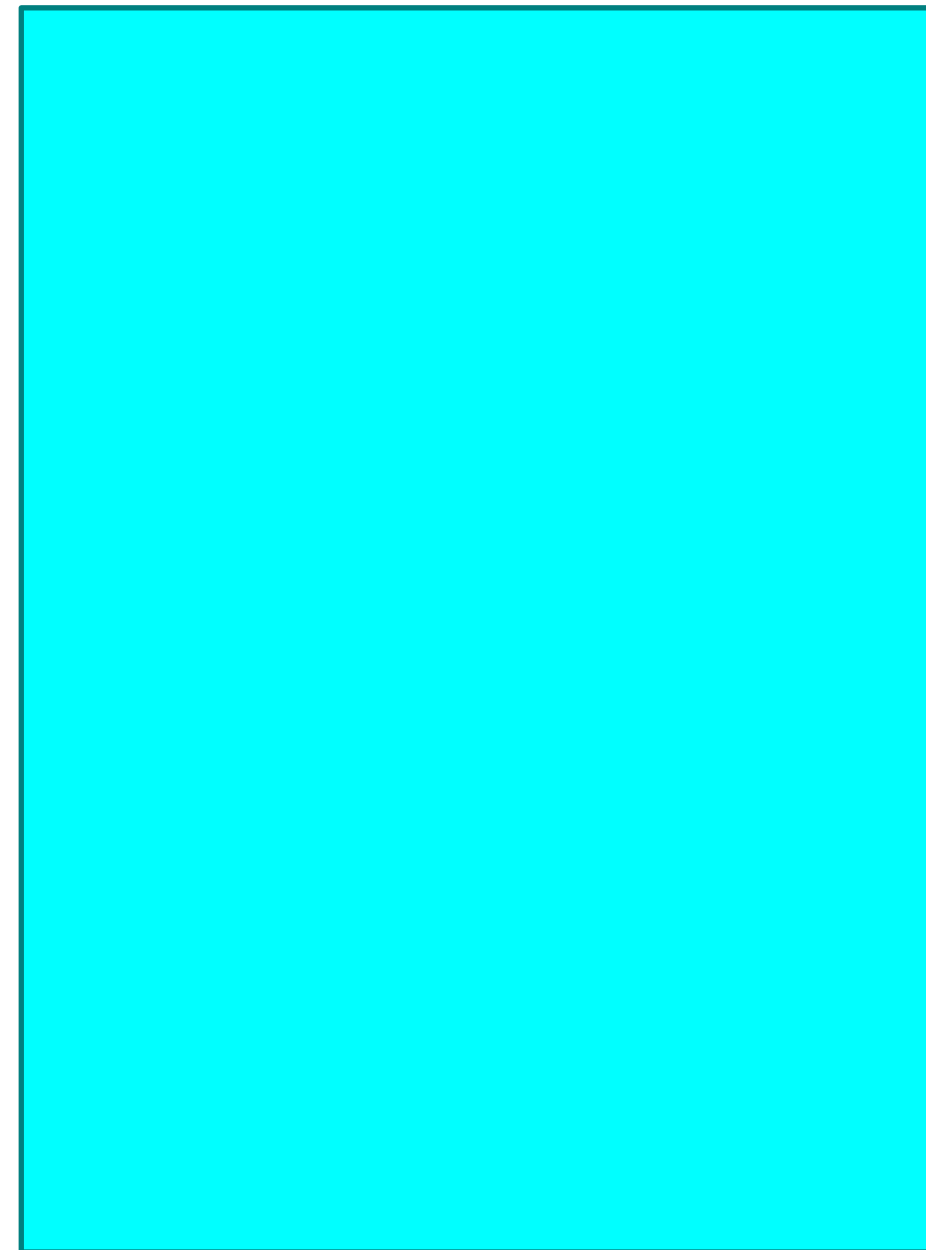
15 K

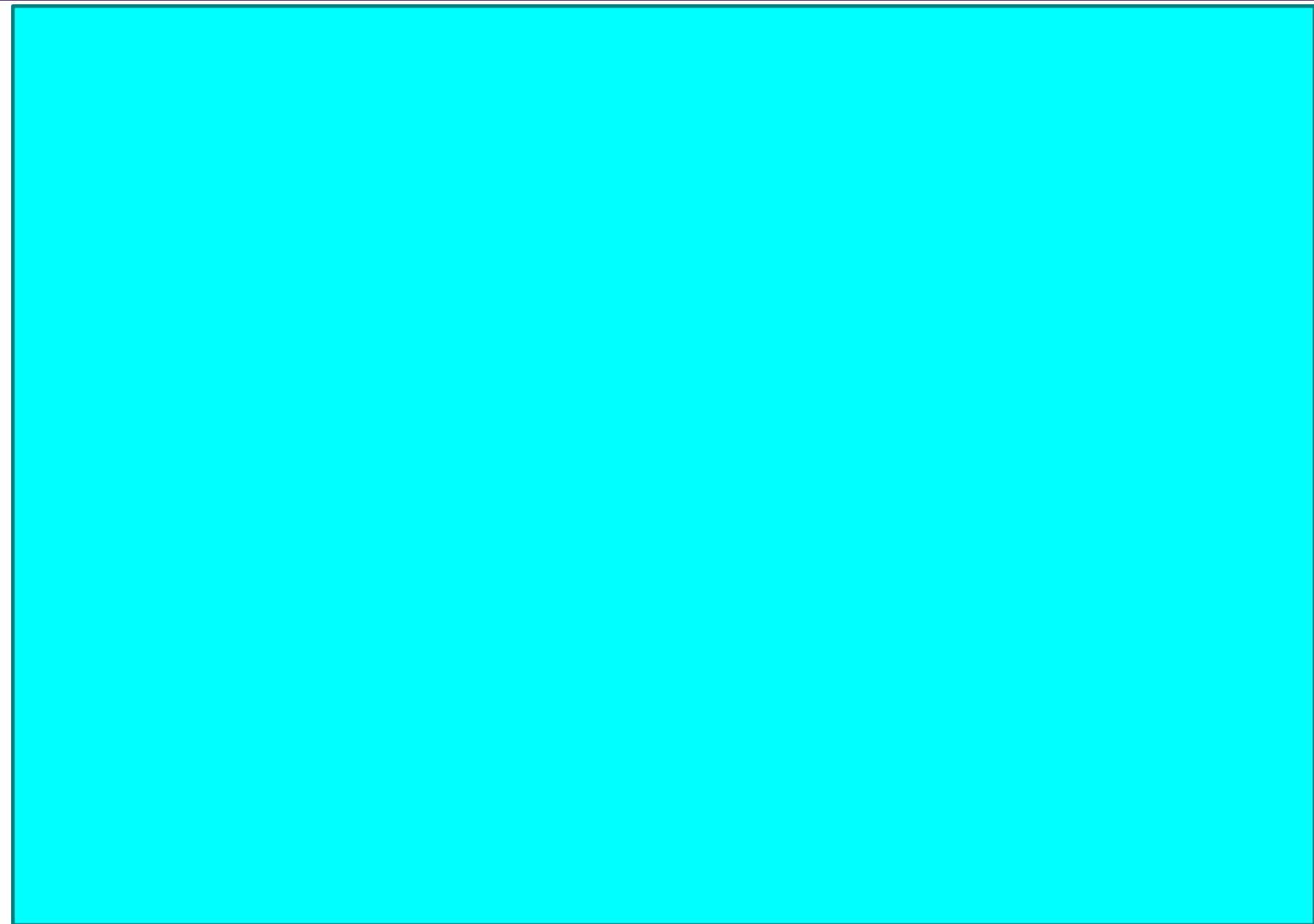


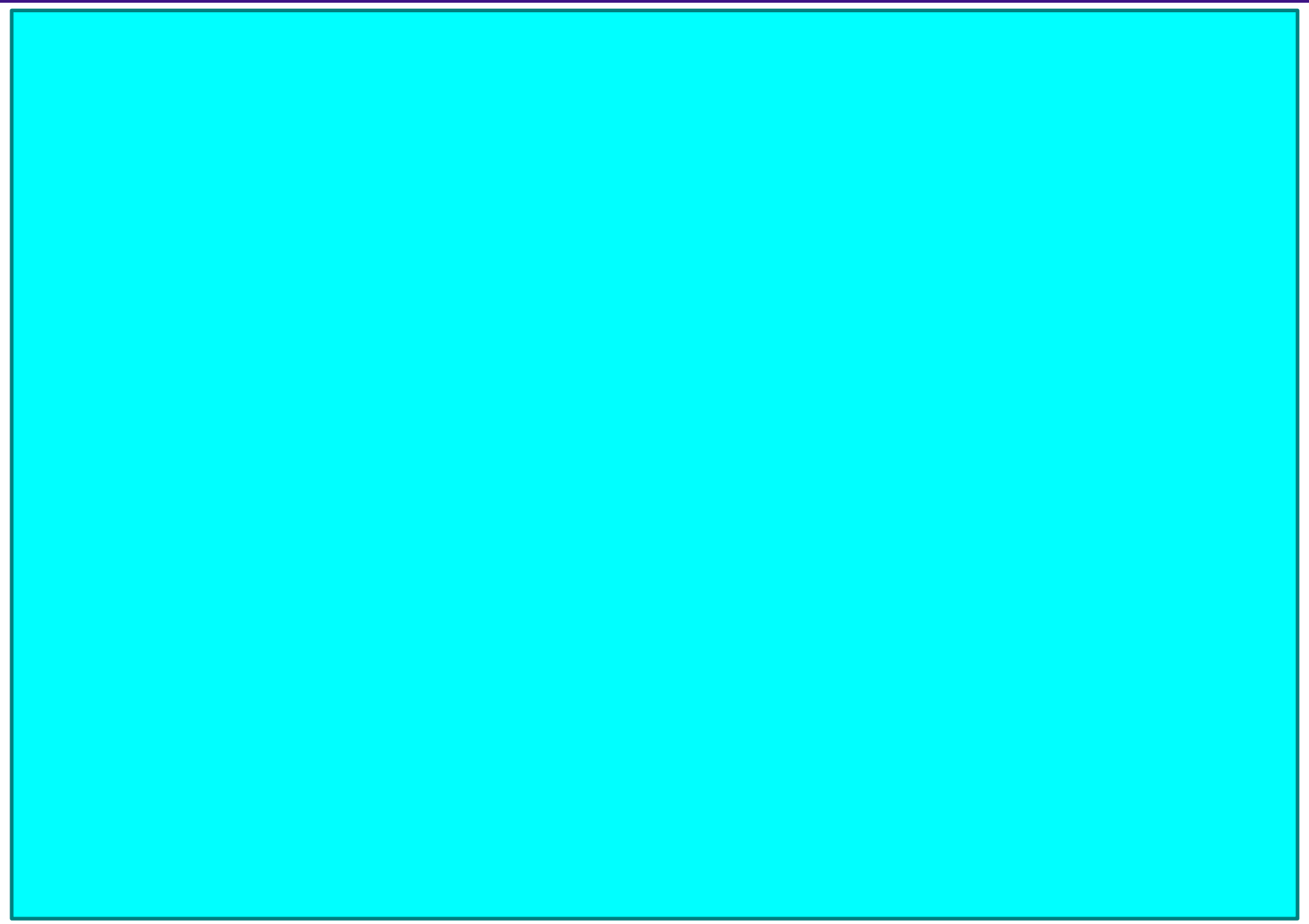
nt (..... egl

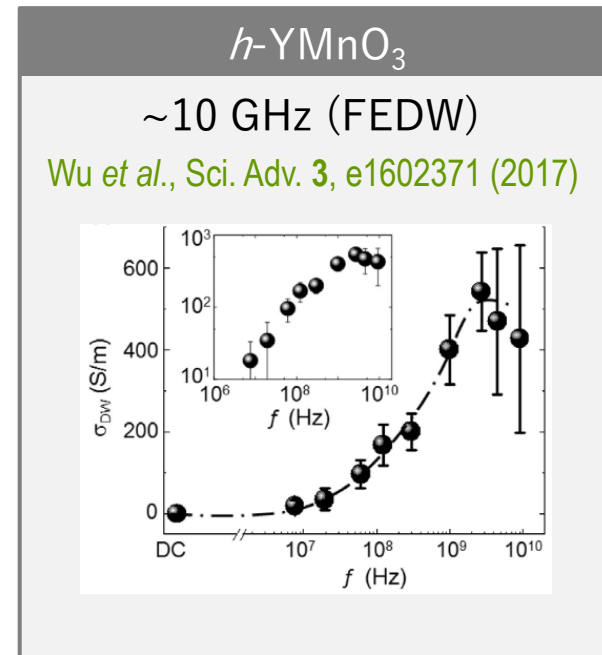
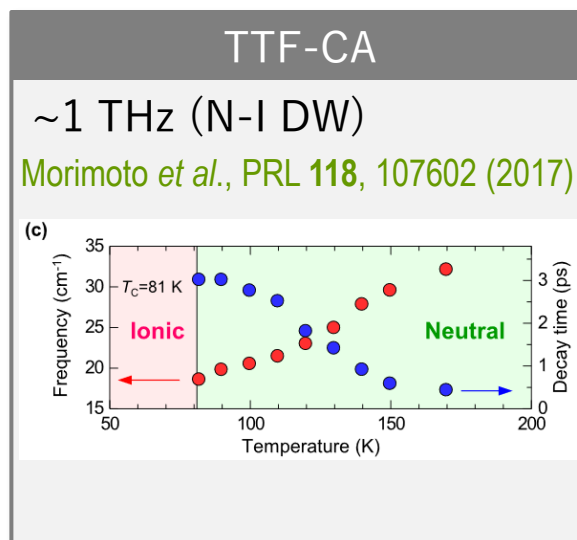
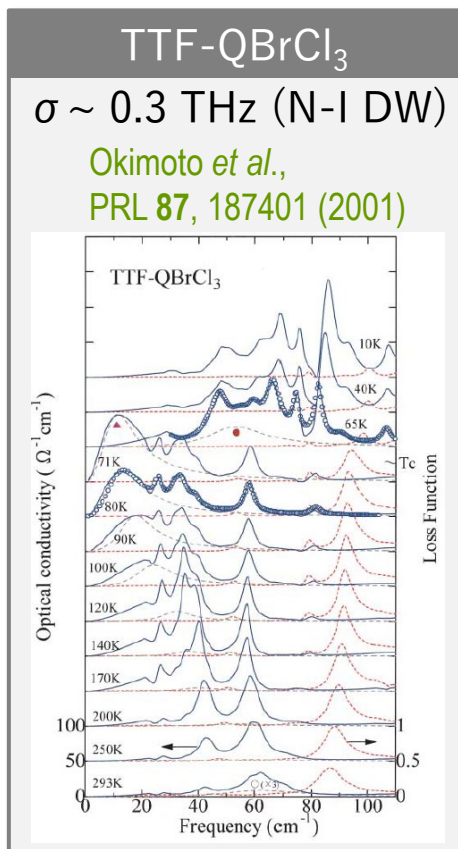
octahedral anions:

tetrahedral anions (anion order (AO)):

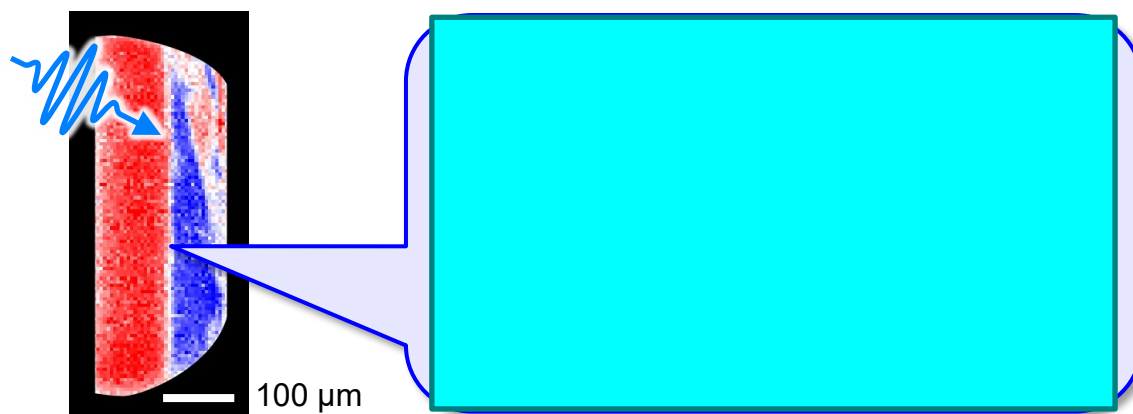






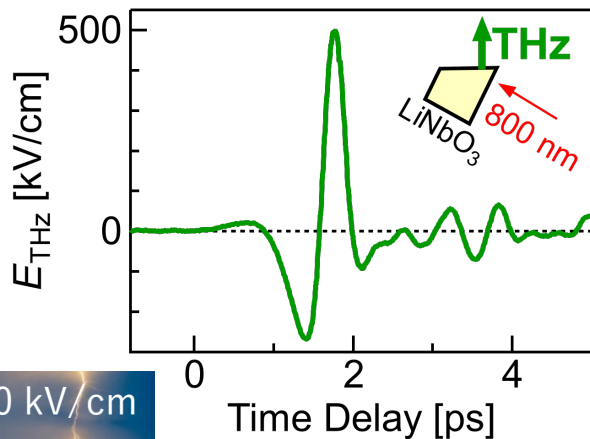


this work:



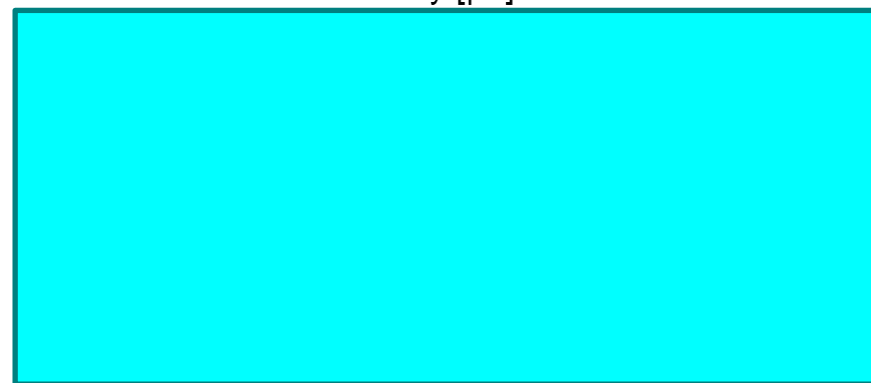
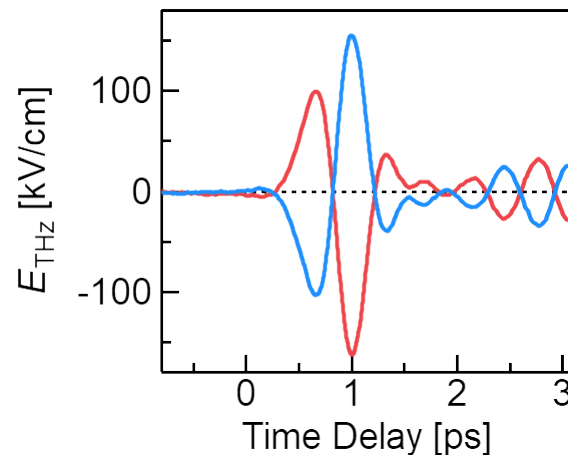
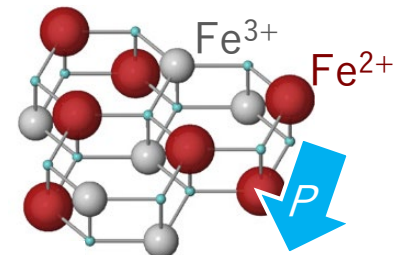
intense THz light: \sim MV/cm

Hebling *et al.*, Opt. Express (2002)
Hirori *et al.*, Appl. Phys. Lett. (2011)



electronic ferroelectrics LuFe₂O₄

Yu, Koshihara, Okimoto (TITECH)
Fujiwara, Ikeda (Okayama Univ.)
Fujiwara *et al.*, Sci. Rep. (2021)

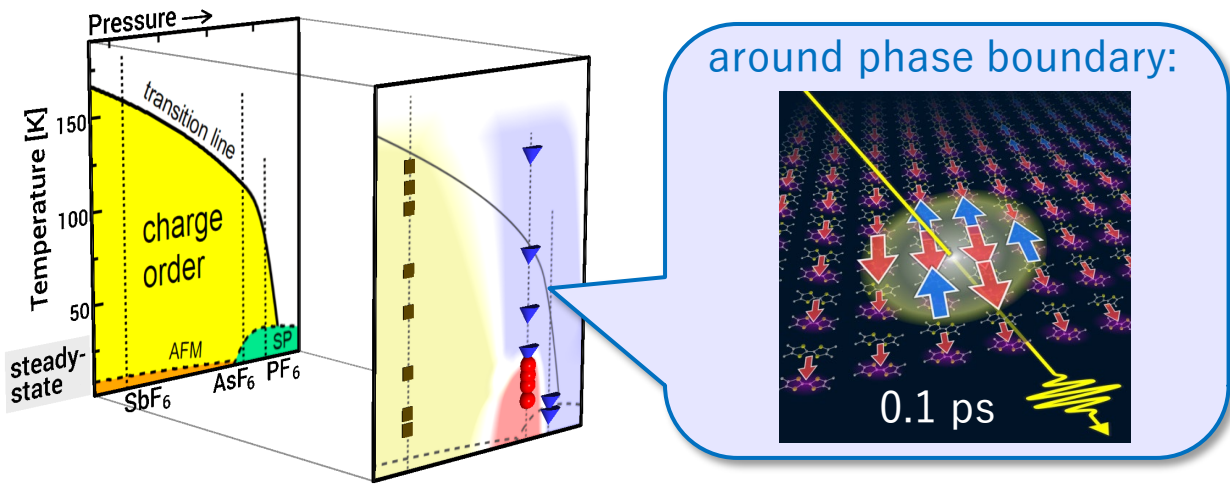


gigantic/ultrafast control

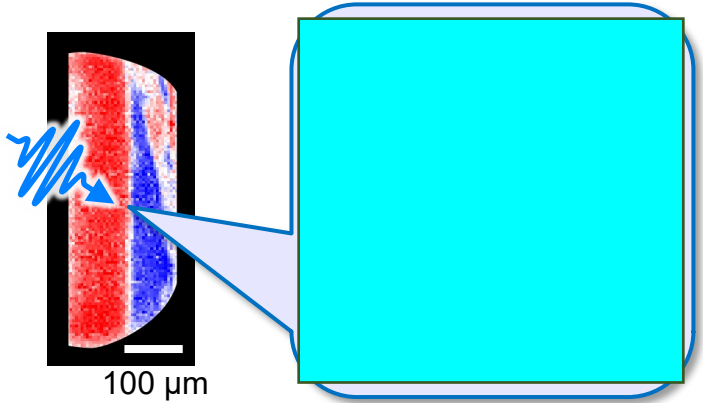
summary (THz dynamics of electronic ferroelectrics, (TMTTF)₂X)

- short-range charge correlations are enhanced upon photoexcitation

Phys. Rev. Res.
3, L032043 (2021)



- macroscopic electronic domains host optical functions



- phase boundary is the key