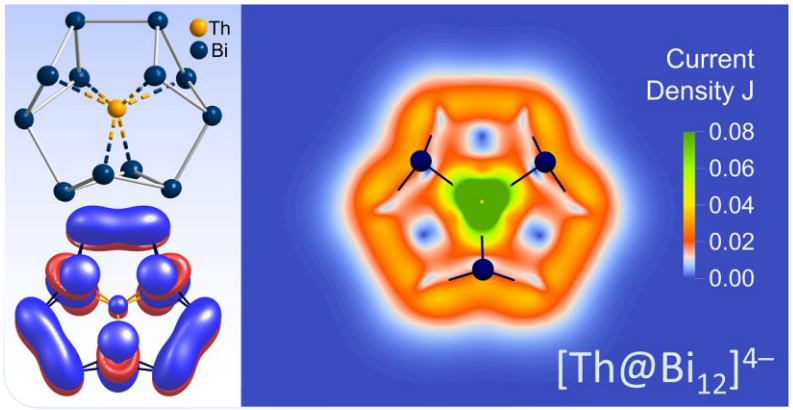
Karlsruhe Institute of Technology

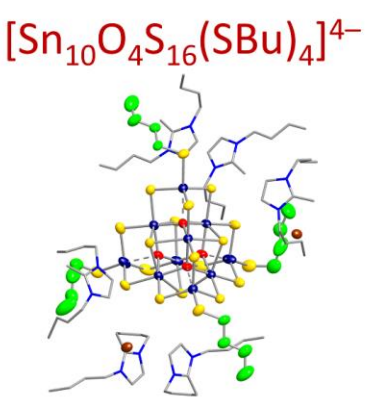
Multinary Clusters as Basis for Uncommon Materials

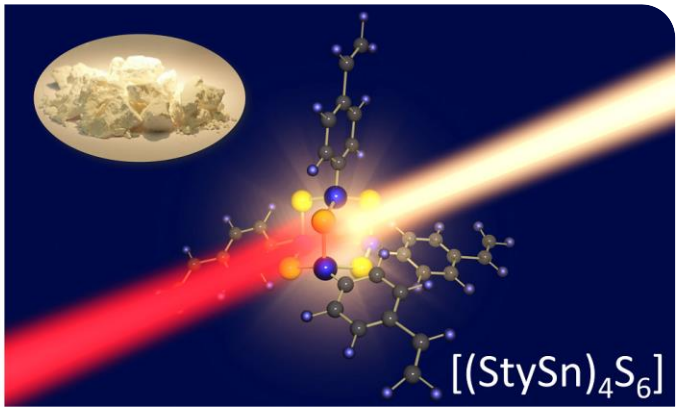
Stefanie Dehnen
Institute of Nanotechnology

Helmholtz-Zentrum hereon

MSE Day
Geesthacht, Nov 14, 2023



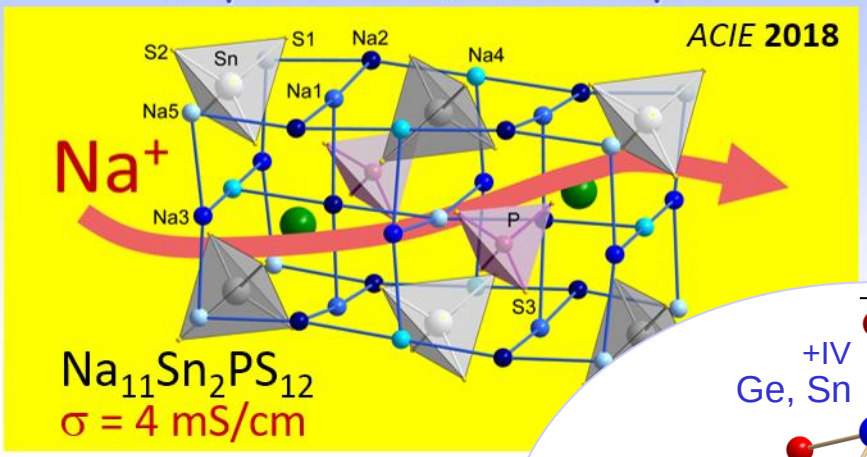




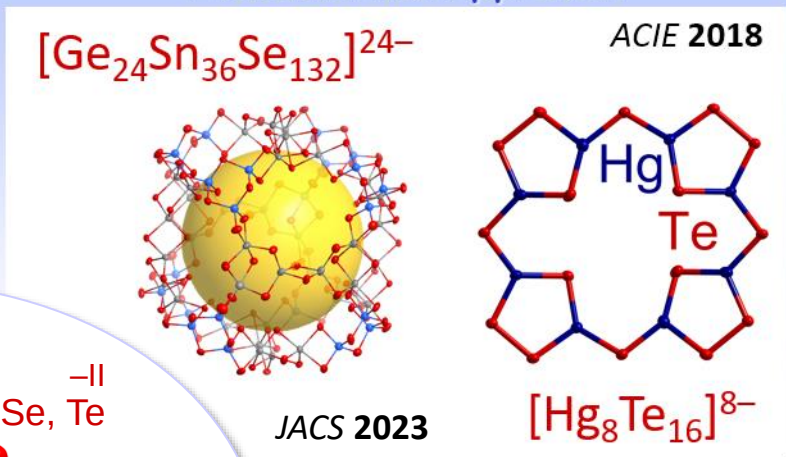
JACS **2013**; *J. Power Sources* **2016**, **2017**; *ACIE* **2018**

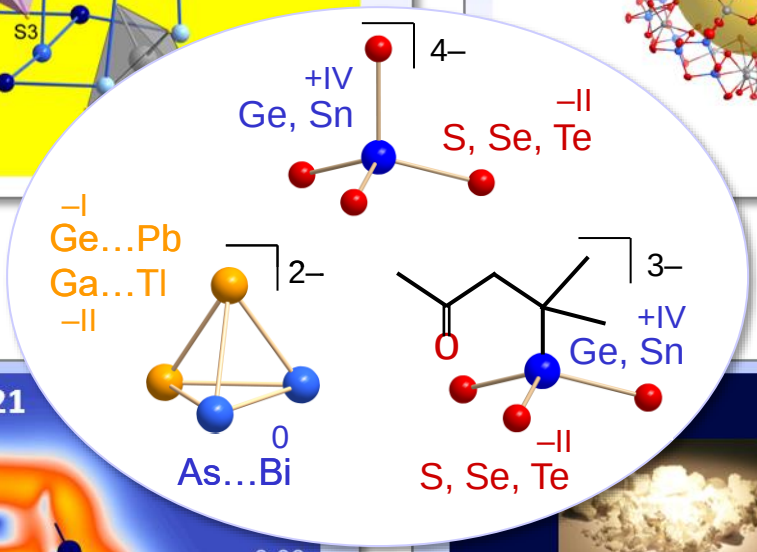
JACS **2023**; *JACS Au* **2022**, *ACIE* **2021**; *Chem. Sci.* **2019**, **2020**

Multinary Chalcogenidometalates
→ Opto-Electronics & Transport



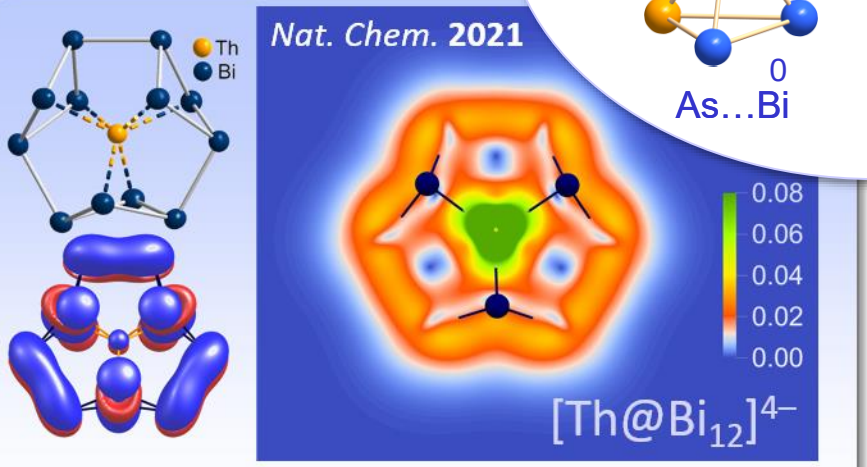
Non-Classical Chalcogenidometalates
→ Ionothermal Approach



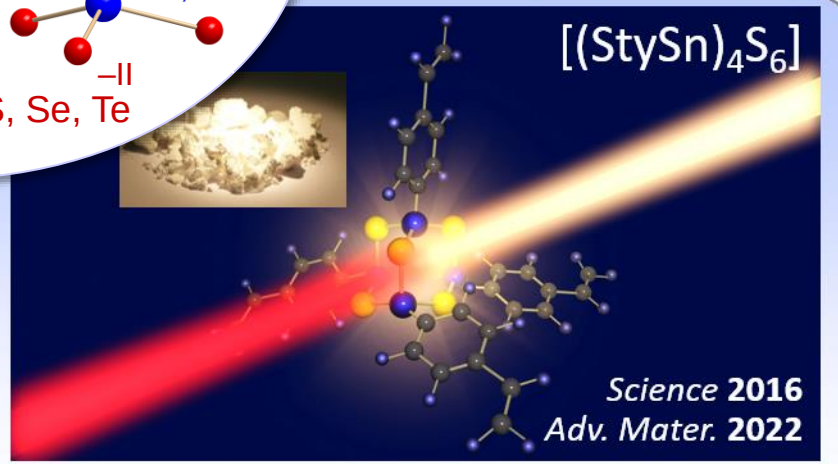


Zeolite Analogs
Multimetallic Clusters

Uncommon Structures
Hybrid Compounds



Zintl Clusters and Polyanions
→ Formation Pathways, Bonding & Reactivity



Organyl Functionalized Cages & Networks
→ Multifunctionality & Molecular Containment

Nat. Chem. **2023**, **2021**; *Nat. Comm.* **2020**; *ACIE* **2023**; *JACS* **2021**

Science **2016**; *JACS* **2019**; *ACIE* **2021**; *Adv. Mater.* **2022**

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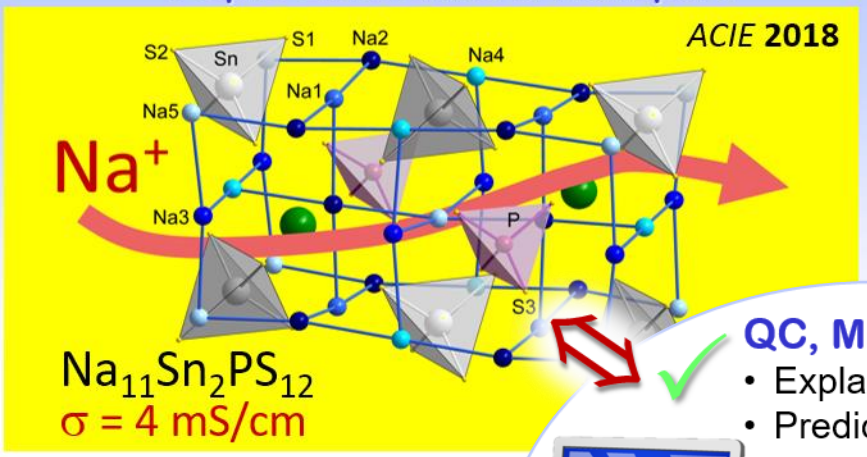
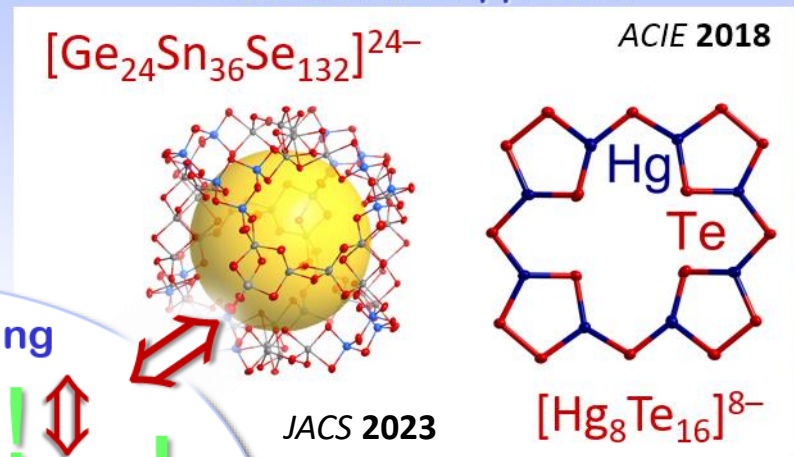


Non-Classical Chalcogenidometalates
→ Ionothermal Approach



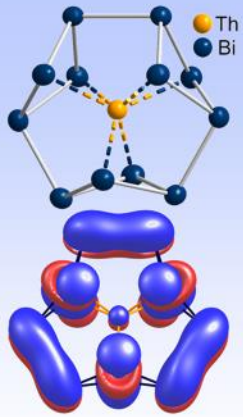
QC, Modelling
- Explanation
- Prediction

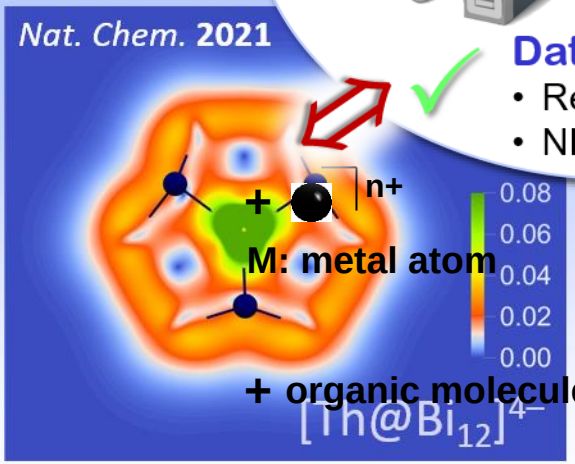
Automation
- High-throughput synthesis, analysis, processing

Data management
- Repositories
- NFDI

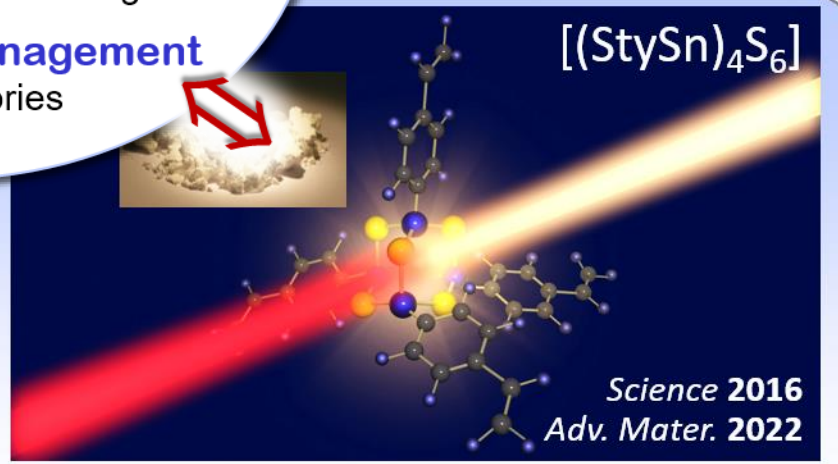
Zeolite Analogs
Multimetallic Clusters

Uncommon Structures
Hybrid Compounds





Zintl Clusters and Polyanions
→ Formation Pathways, Bonding & Reactivity



Organyl Functionalized Cages & Networks
→ Multifunctionality & Molecular Containment

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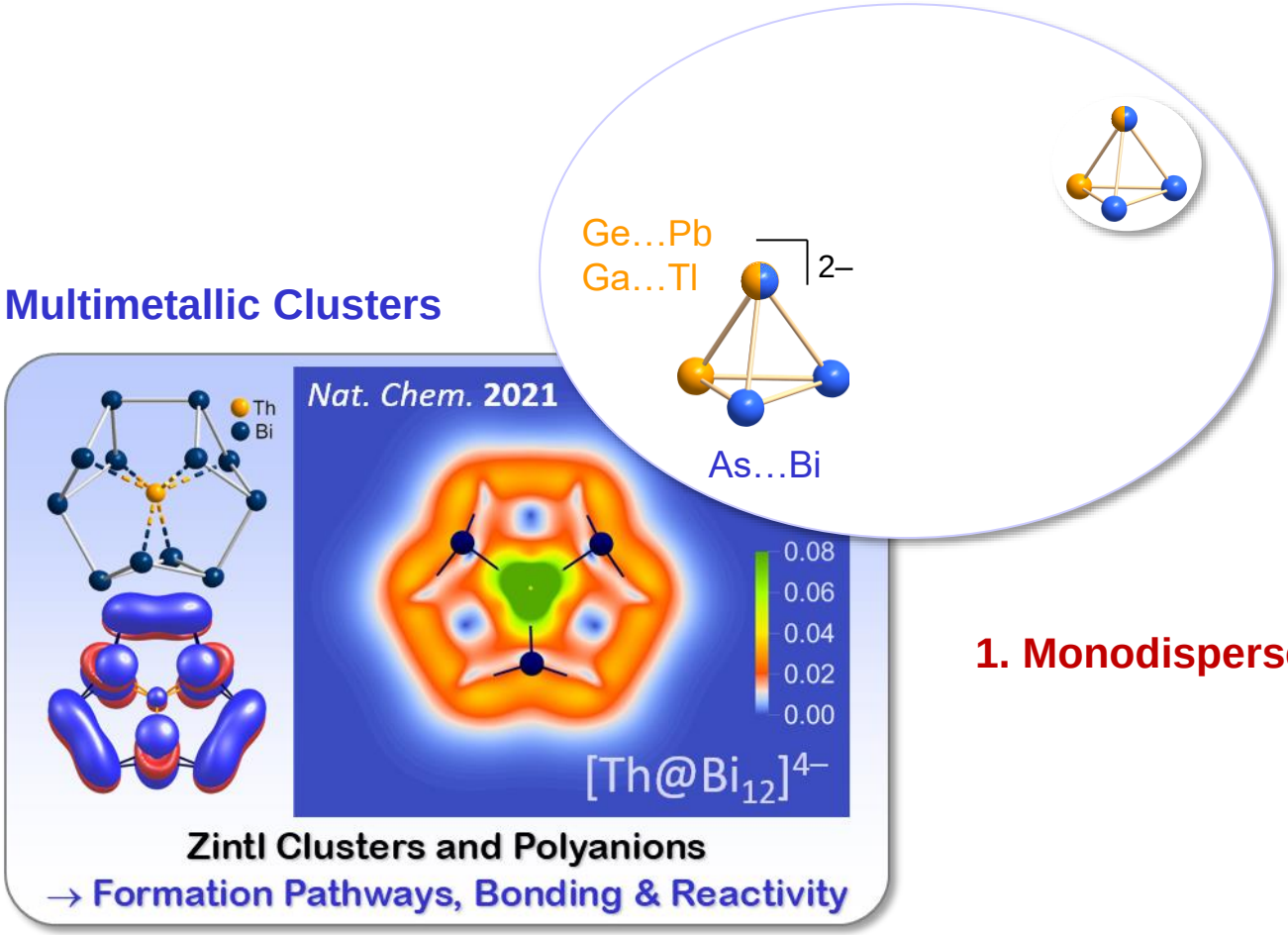
Science **2016**; *JACS* **2019**; *ACIE* **2021**; *Adv. Mater.* **2022**

Multimetallic Clusters

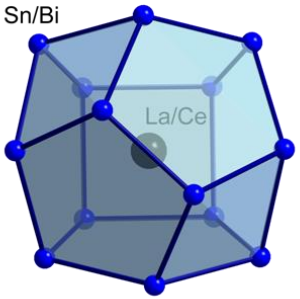


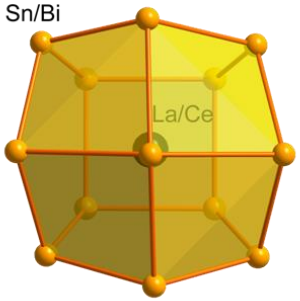
1. Monodisperse Molecular Alloys

Review: R. J. Wilson, N. Lichtenberger, B. Weinert, SD, *Chem. Rev.* **2019**, *119*, 8506–8554.

JACS **2012**
Angew. Chem. **2014**
Chem. Eur. J. **2015**

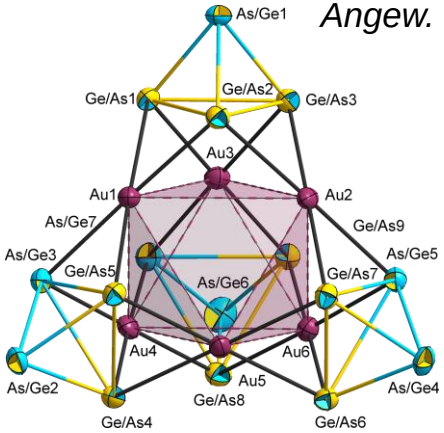
Angew. Chem. **2011**
Chem. Commun. **2015**
Nat. Comm. **2016**

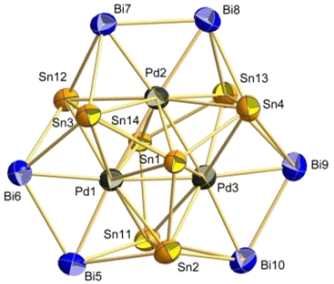




Non-Δ-hedral cages

Angew. Chem. **2020**



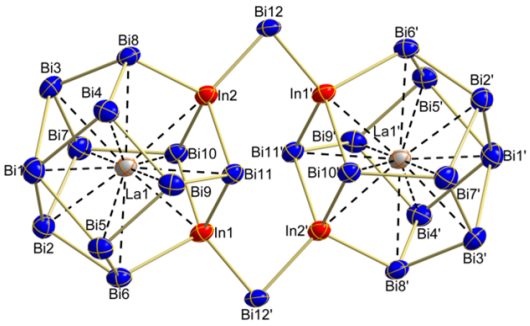


JACS **2011**
Nat. Chem. **2012**
Chem. Commun. **2018**

Sn,Pb/Sb,Bi/Ln^{3+}
Ge/As/M^{5+}

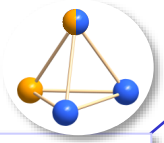
Ge/As/Au^{I}

Sn/Bi/Pd^{0}



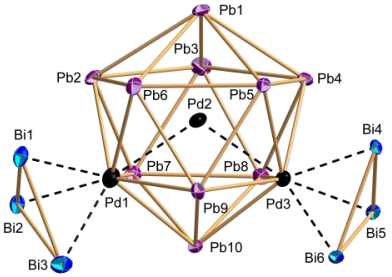
Chem. Eur. J. **2012**
Angew. Chem. **2014**

In/Bi/La^{3+}
Ga/Bi/La^{3+}



$[K(crypt)]_z[T_xE_y]$

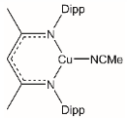
Pb/Bi/Pd^{0}



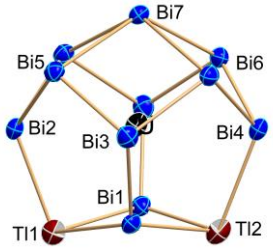
Angew. Chem. **2013**

Ga,Tl/Bi/U^{3+}
Ga/Bi/Th^{4+}

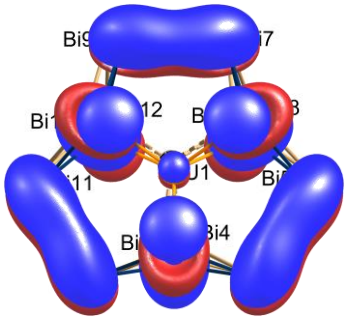
Pb/Sb/Au^{I}
Sn/Sb/Cu^{I}



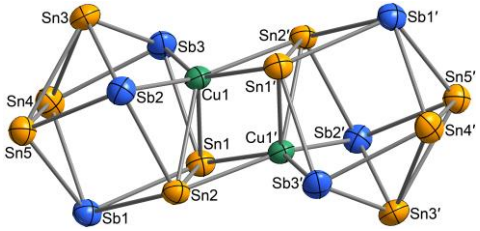
Sn,Pb/Sb,Bi/Co^{-},Ni^{0}



JACS **2016**



Nat. Chem. **2021**



Angew. Chem. **2016**
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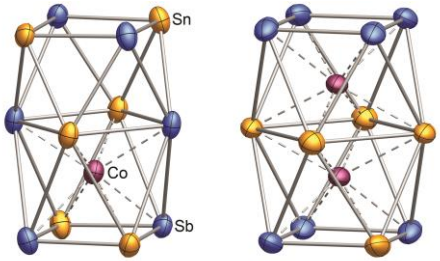

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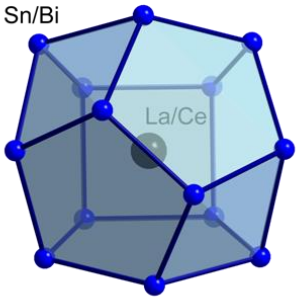
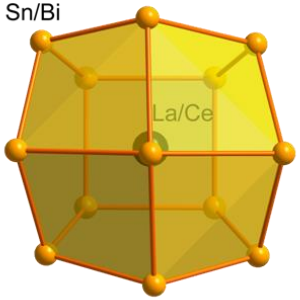
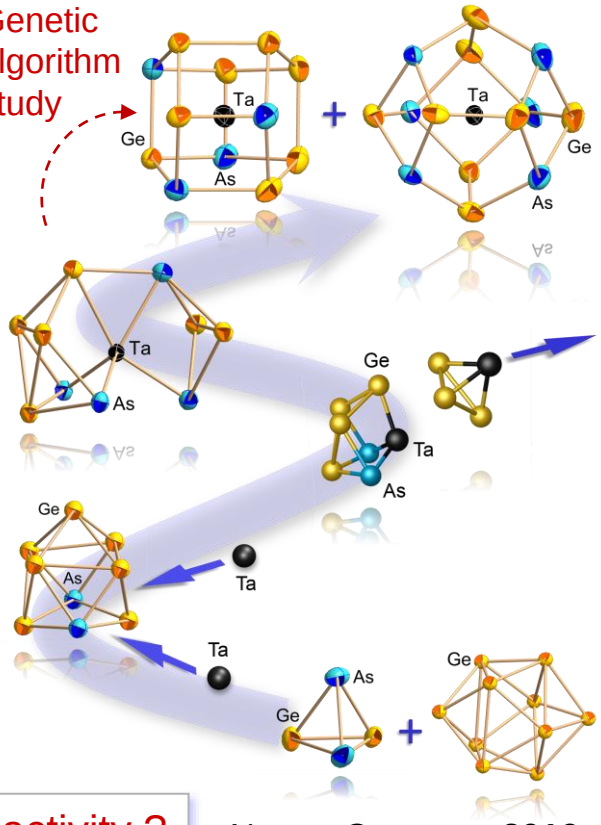
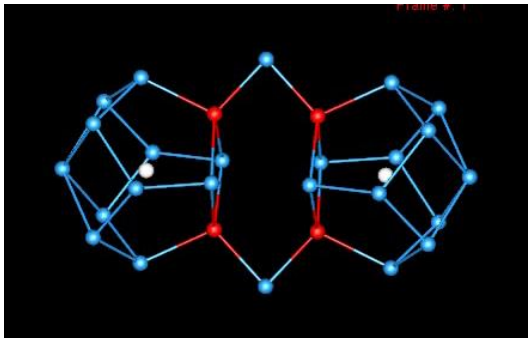




Non-Δ-hedral cages

Genetic algorithm study





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$Sn,Pb/Sb,Bi/Ln^{3+}$
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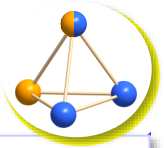
Formation ?



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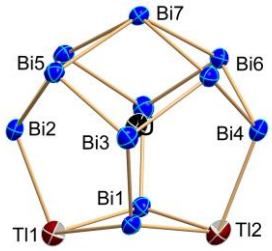
Electronic Structure & Reactivity ?

Nature Commun. **2016**



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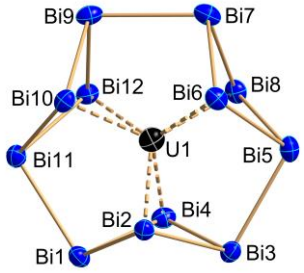
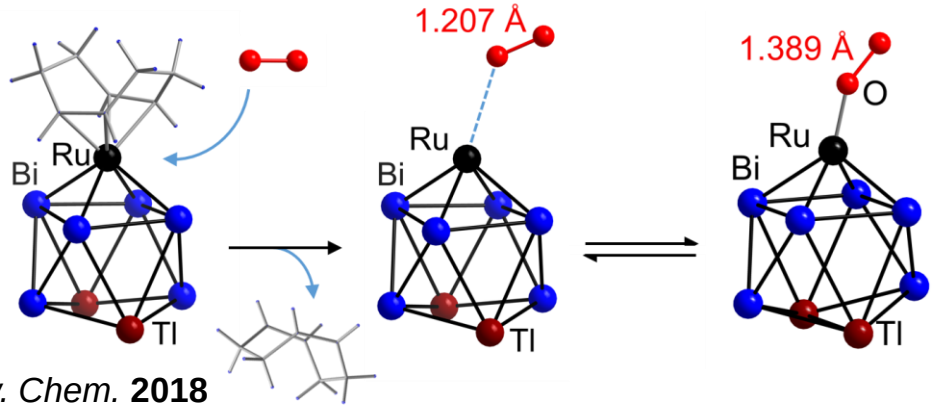


Nature Chem. **2021**



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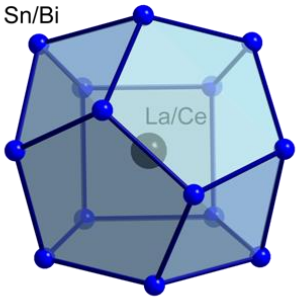

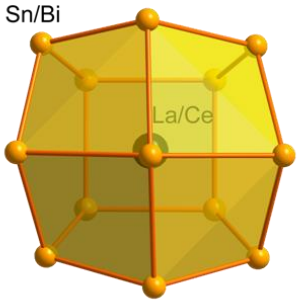

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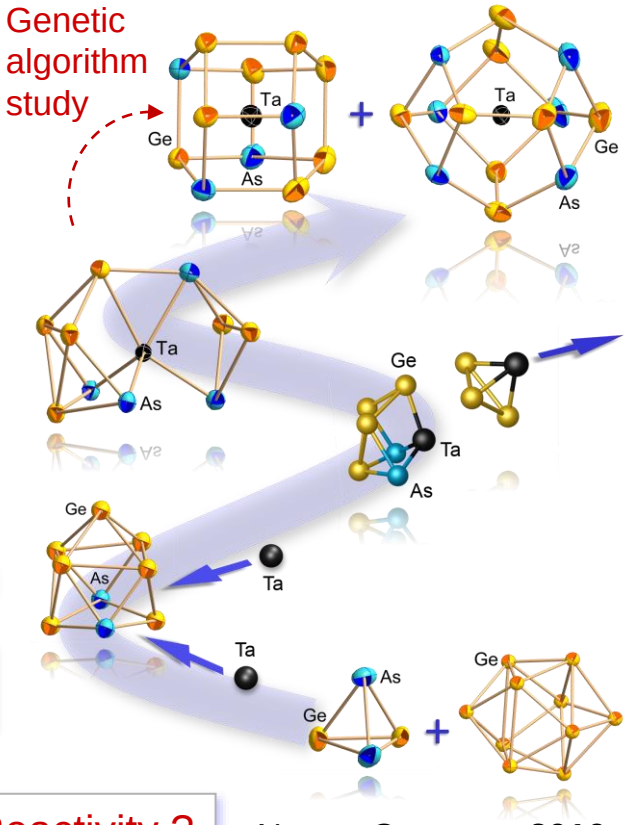

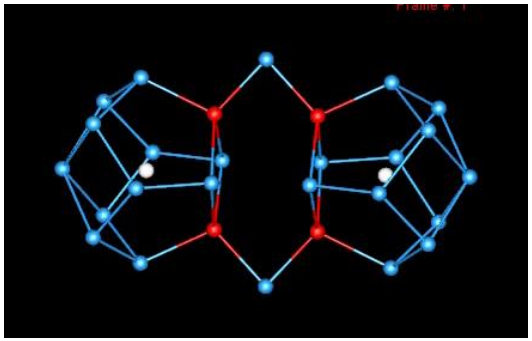

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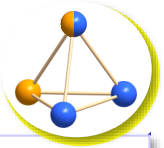

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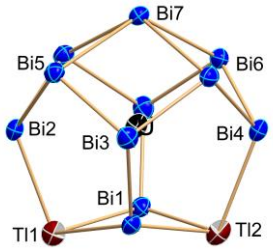
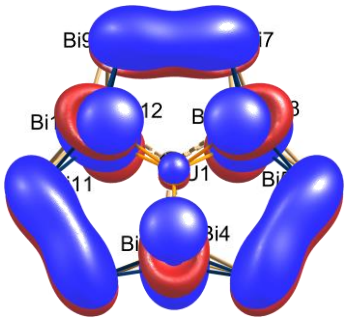
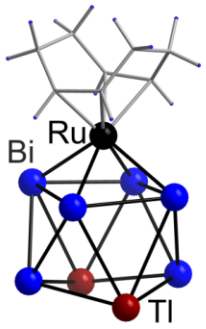


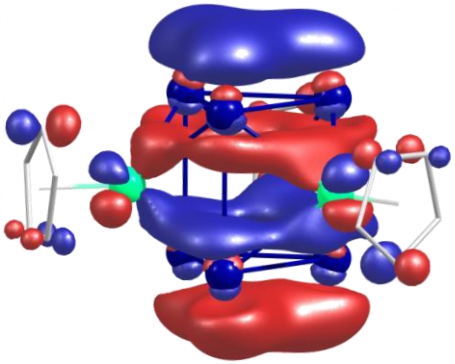
JACS **2016**



Nature Chem. **2021**



Angew. Chem. **2018**



Nature Chem. **2023**

New metal aromaticity

Review: R. J. Wilson, N. Lichtenberger, B. Weinert, SD, *Chem. Rev.* **2019**, *119*, 8506–8554.

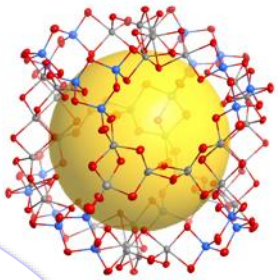
JACS **2023**; *JACS Au* **2022**, *ACIE* **2021**; *Chem. Sci.* **2019**, **2020**

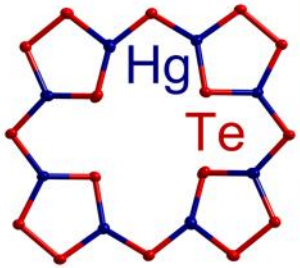
2. (Soluble) Semiconductor Clusters

Non-Classical Chalcogenidometalates

→ Ionothermal Approach

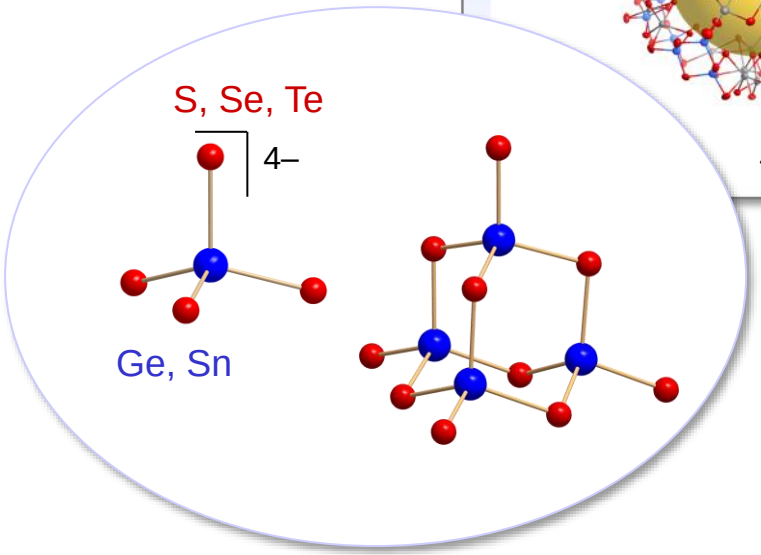
$[Ge_{24}Sn_{36}Se_{132}]^{24-}$ *ACIE* **2018**





JACS **2023**

$[Hg_8Te_{16}]^{8-}$



Uncommon Structures

Ionothermal Syntheses

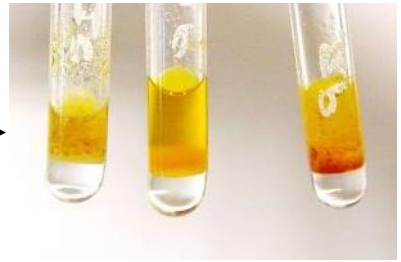
ionic liquids: salts with melting points ≤ 100°C

→ “designer solvents”

ionothermal:

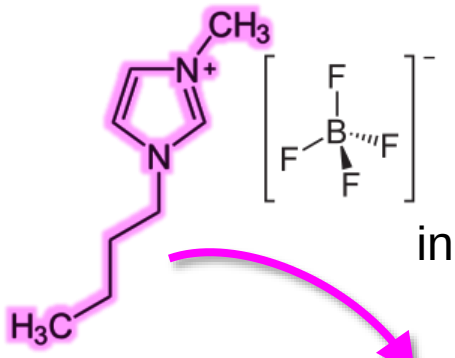
80°…150°C

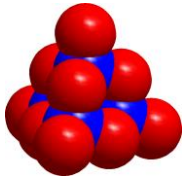
1-4 days



→ solid state synthesis „near room temperature“

binary precursor: $K_4[Ge_4Se_{10}] + 5\ SnCl_4$

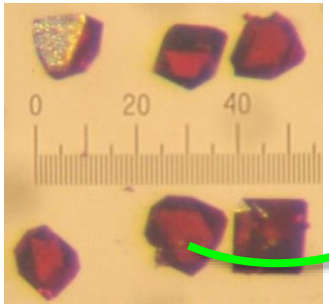


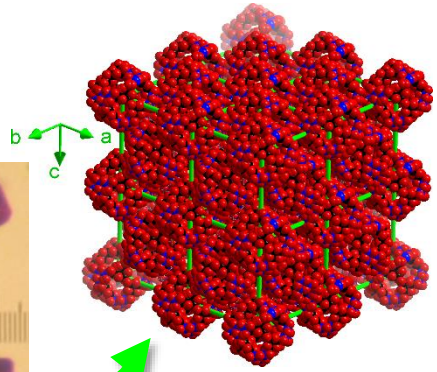


in $(C_4C_1Im)[BF_4]$

150°C, 3 d

$(C_4C_1Im)_{24}[Ge_{24}Sn_{36}Se_{132}]$





Y. Lin, W. Massa, SD, *J. Am. Chem. Soc.* **2012**, *134*, 4497–4500.

Ionothermal Syntheses

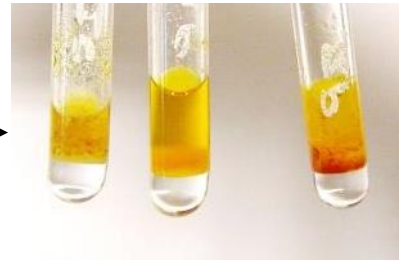
ionic liquids: salts with melting points ≤ 100°C

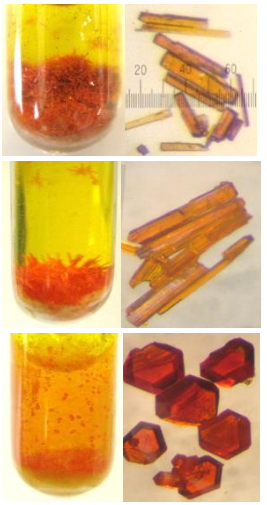
→ “designer solvents”

ionothermal:

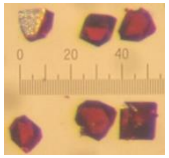
80°…150°C

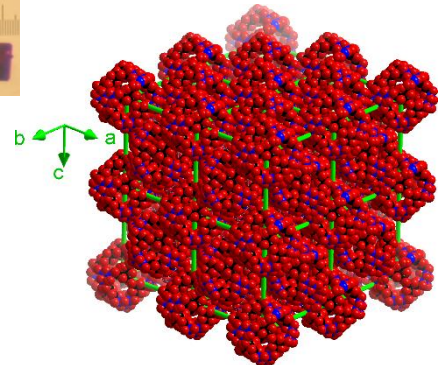
1-4 days

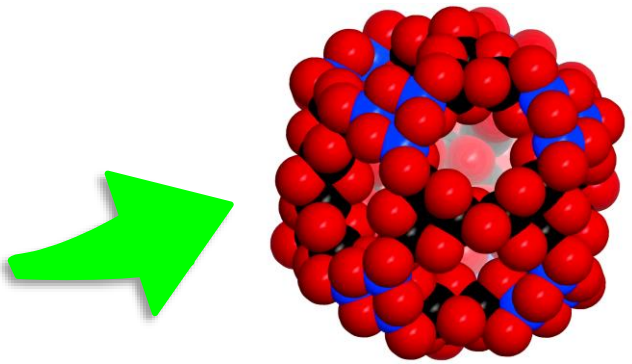




→ solid state synthesis „near room temperature“







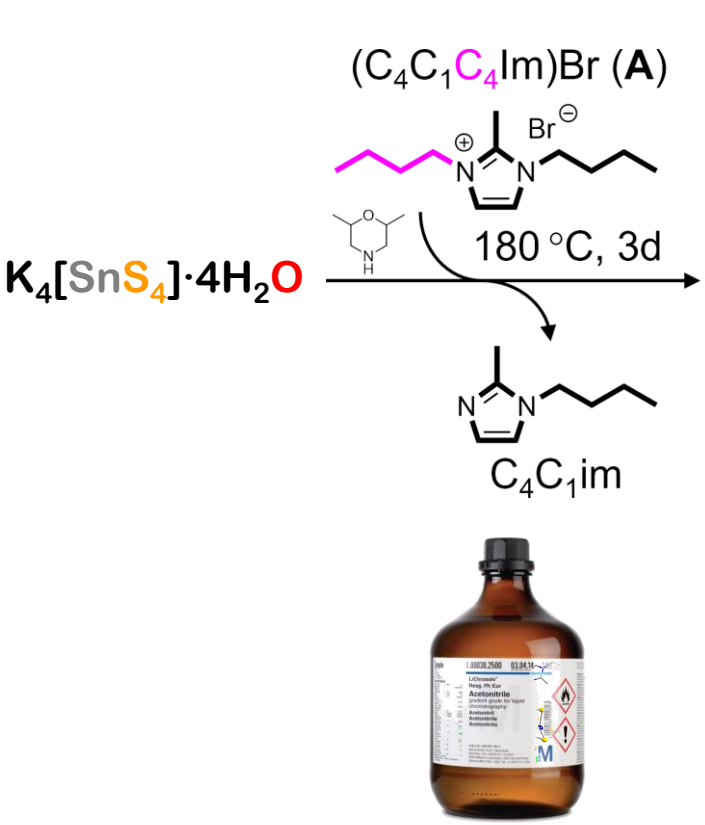
$(C_4C_1Im)^+_{24}[Ge_{24}Sn_{36}Se_{132}]^{24-}$

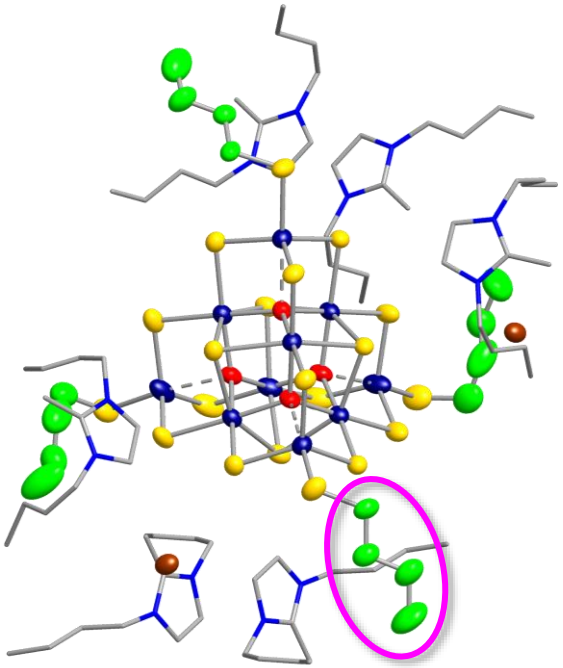
high charge ⇒ insoluble

Y. Lin, W. Massa, SD, *J. Am. Chem. Soc.* **2012**, *134*, 4497–4500.

Well-Soluble Semiconductor Clusters

selective butyl transfer: charge & polarity reduction





$[Sn_{10}S_{16}O_4(SBu)_4]^{4-}$

cf. $[Sn_{10}S_{20}O_4]^{8-}$

W. Schiwy, B. Krebs, *Angew. Chem.* **1975**, *87*, 451-452.

→ high solubility in CH_3CN ! ⇒ retention of semiconductor properties ?

R = decyl

R = propyl, pentyl, hexyl

M. Tallu, B. Peters, A. Friedrich, SD, *Inorg. Chem.* **2023**, *62*, 13943.

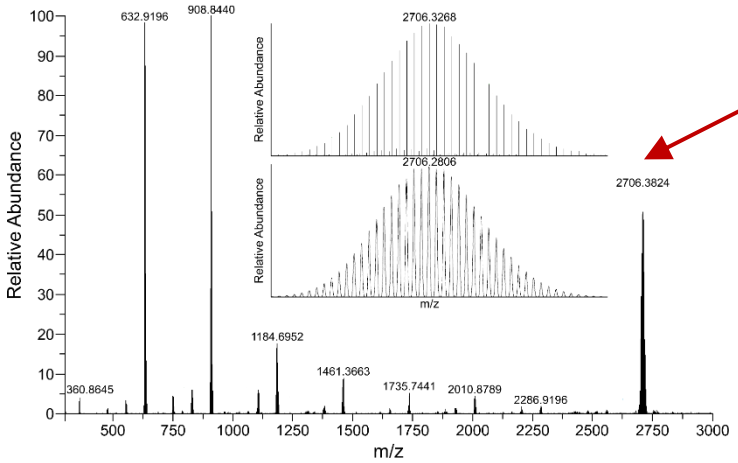
G. Stuhrmann, J. Schneider, K. Schmidt, SD, *Chem. Commun.* **2023**, *59*, 13171–13174.

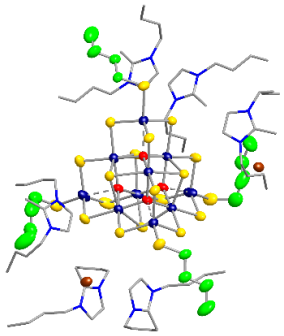
B. Peters, G. Stuhrmann, F. Mack, F. Weigend, SD, *Angew. Chem. Int. Ed.* **2021**, *60*, 17622–17628.

Well-Soluble Semiconductor Clusters

Karlsruhe Institute of Technology

solution studies in CH_3CN: ESI-MS





$\{(C_4C_1C_4Im)_3[Sn_{10}O_4S_{16}(SBu)_4]\}^-$

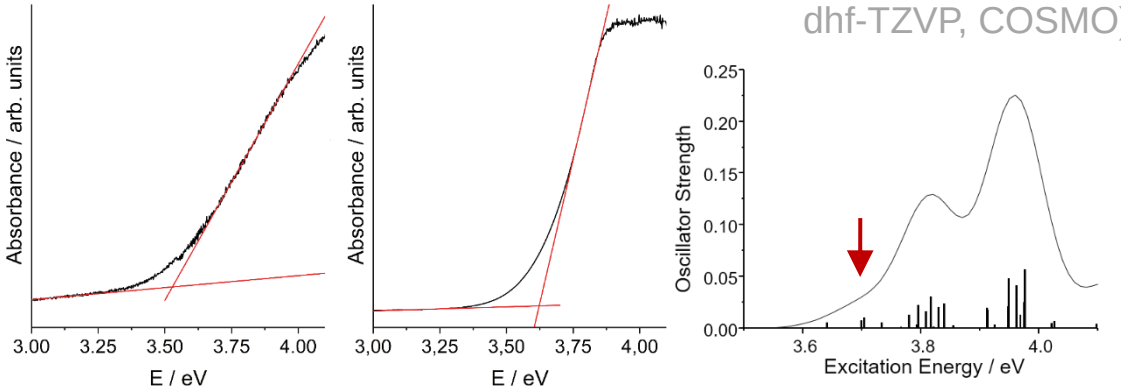
→ clusters retained in solution

UV-visible spectra:

solid state

solution
(2 mmol/L in CH_3CN)

TD-DFT
(TURBOMOLE, PBE0, dhf-TZVP, COSMO)



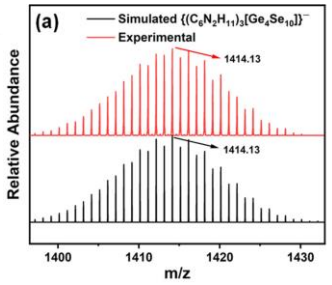
→ semiconductor-like optical gap persists !

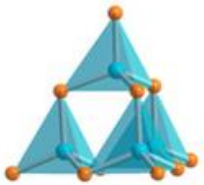
B. Peters, G. Stuhrmann, F. Mack, F. Weigend, SD, *Angew. Chem. Int. Ed.* **2021**, *60*, 17622–17628.

Well-Soluble Semiconductor Cluster Oligomers

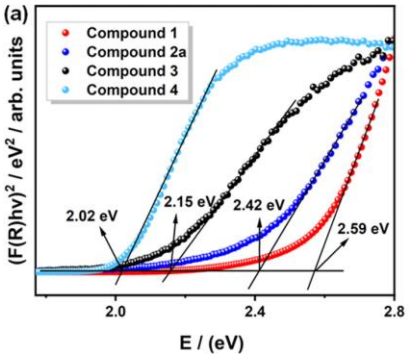
Karlsruhe Institute of Technology

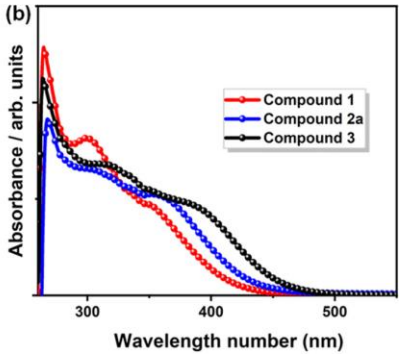
charge reduction by aggregation





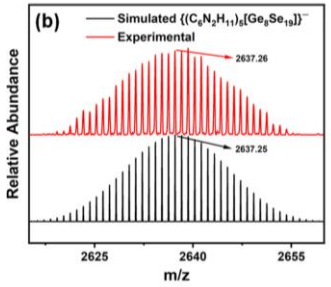
0D-$[Ge_4Se_{10}]^{4-}$

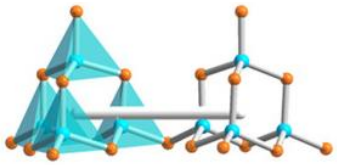




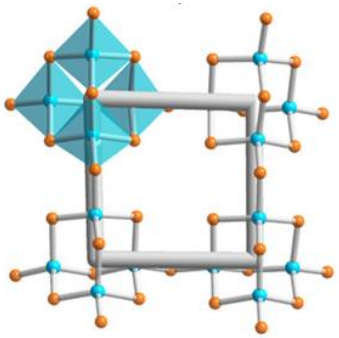
UV-vis: solid state

UV-vis: DMF solution



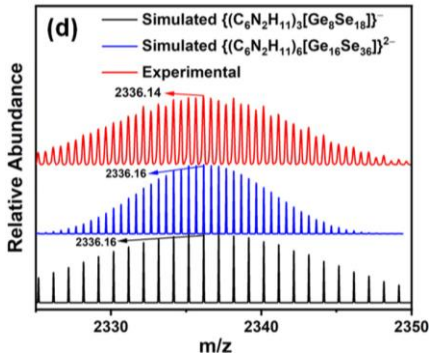


0D-$[Ge_8Se_{19}]^{6-}$



0D-$[Ge_{16}Se_{36}]^{8-}$

ESI-MS from DFM solution



→ semiconductor-like optical gap retained in solution

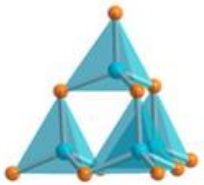
Z. Wu, I. Nußbruch, S. Nier, SD, *JACS Au* **2022**, 2, 204−213

Selective Cation Capture by Cluster Oligomers

Karlsruhe Institute of Technology

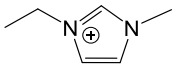
Cs^+-selective crystallization

	/	CsCl	NaCl	KCl	RbCl	NaCl CsCl
$[Li_4(H_2O)_{20.33}][Ge_4Se_{10}]$	×	✓	×	×	×	✓
$Na_4[Ge_4Se_{10}]$	×	✓	×	×	×	✓
$[K_4(H_2O)_3][Ge_4Se_{10}]$	×	✓	×	×	×	✓
$Rb_4[Ge_4Se_{10}]$	×	✓	×	×	×	✓
$[Cs_4(H_2O)][Ge_4Se_{10}]$	✓	✓	✓	✓	✓	✓



$A_4[Ge_4Se_{10}]$

A = K



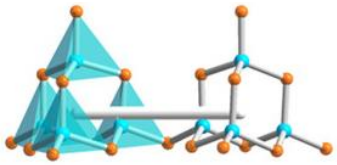
$(C_2C_1Im)[B(CN)_4]$: DMMP

(10 : 1)

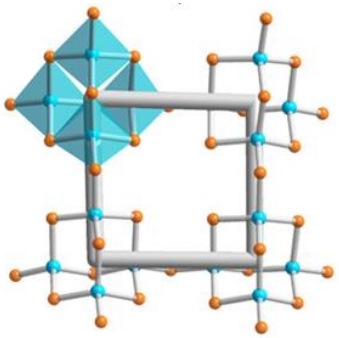
(2 : 1)

A = Cs

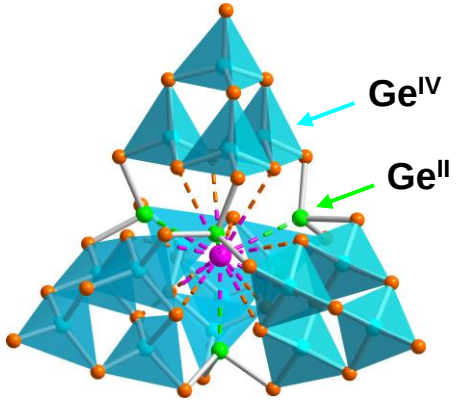
(10 : 1)



$0D\text{-}[Ge_8Se_{19}]^{6-}$



$0D\text{-}[Ge_{16}Se_{36}]^{8-}$

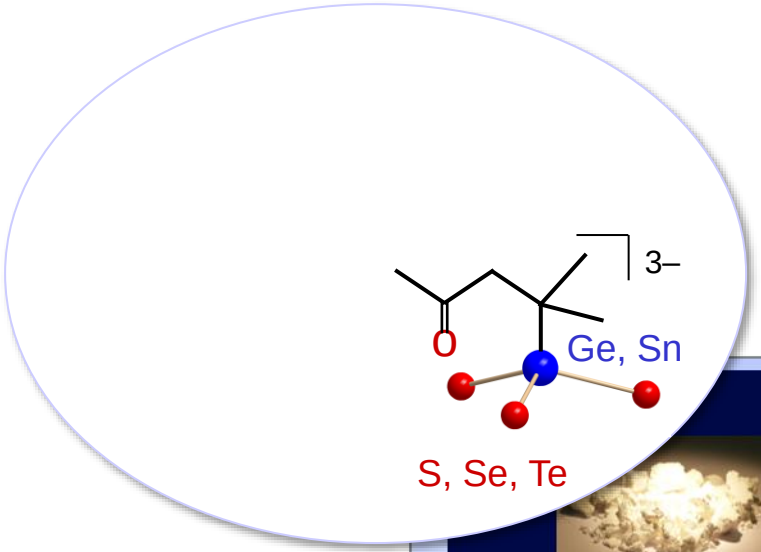


$0D\text{-}[Cs@Ge^{II}_4(Ge^{IV}_4Se_{10})_4]^{7-}$

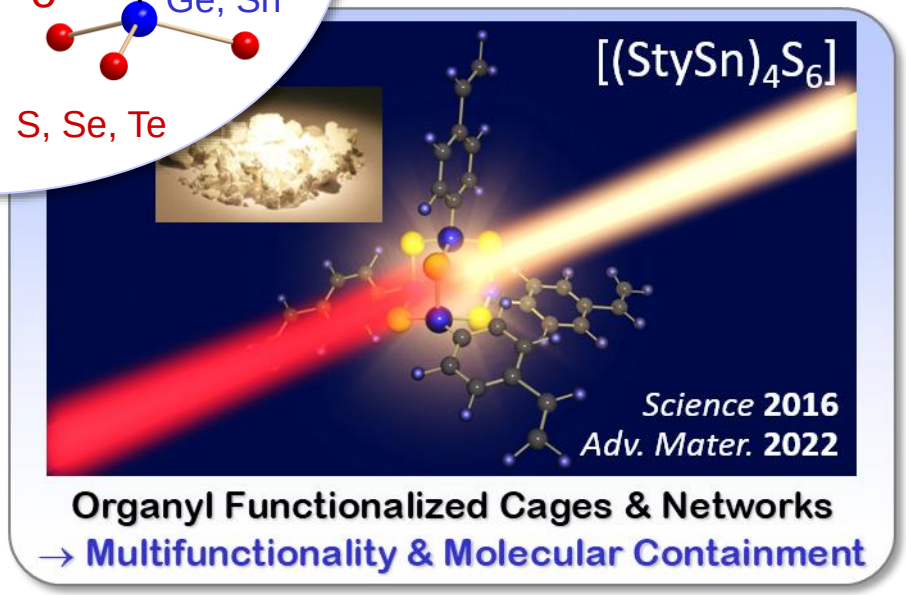
→ internal charge-reduction ⇒ again higher solubility

Z. Wu, F. Weigend, D. Fenske, T. Naumann, J. M. Gottfried, SD, *J. Am. Chem. Soc.* **2023**, 145, 6, 3802–3811.

3. New Emissive Cluster Materials



Hybrid Compounds

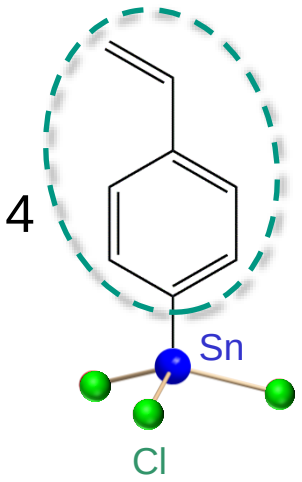


Science **2016**; *JACS* **2019**; *ACIE* **2021**; *Adv. Mater.* **2022**

Hybrid Compounds ⇒ New Emissive Materials

Karlsruhe Institute of Technology

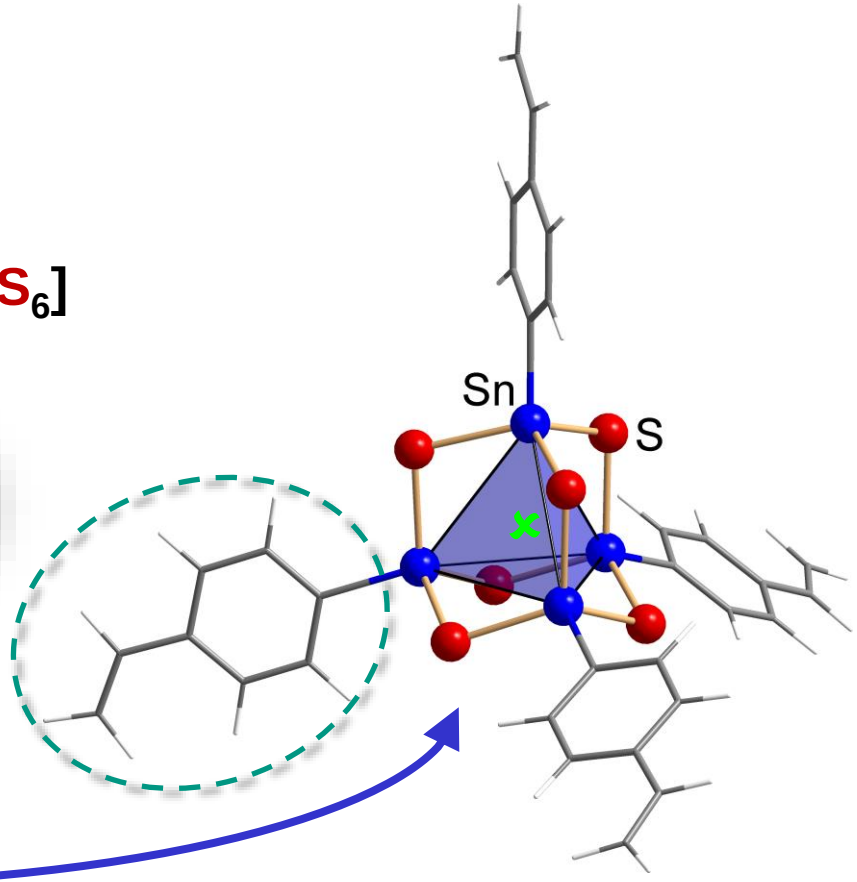
styryl groups @ Sn/S cluster



+ 6 Na_2S

– 12 NaCl

$[(R^{Sty}Sn)_4S_6]$



TURBOMOLE, BP-86, def2-TZVP

amorphous powder, air-stable

ESI-MS: $[(R^{Sty}Sn)_4S_6]$ ✓

DFT: molecular structure

→ styryl ligands ⇒ attachment to semi-conductor surfaces ✓

→ no inversion symmetry ⇒ non-linear optics ?

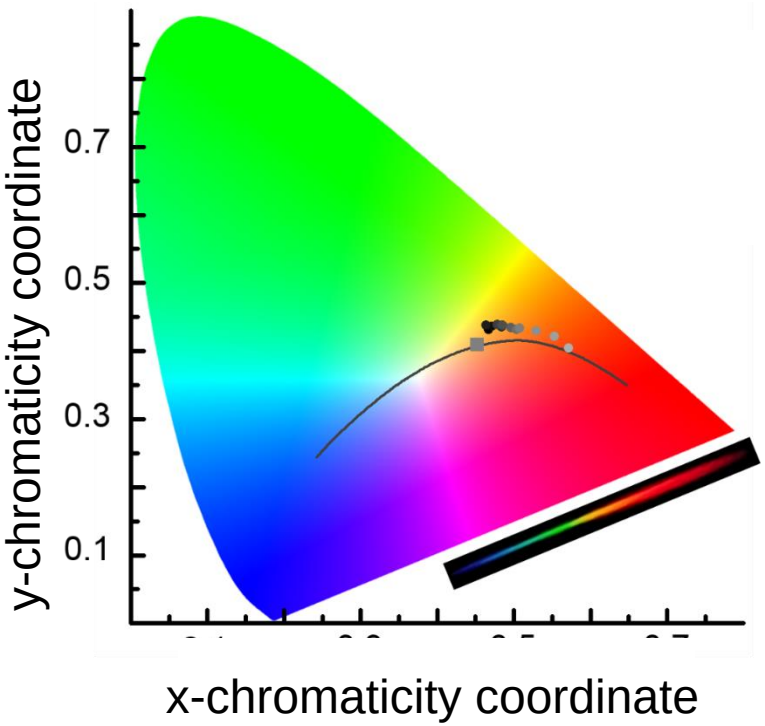
N. W. Rosemann, J. P. Eußner, A. Beyer, S. W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* **2016**, *352*, 301.

$[(R^{Sty}Sn)_4S_6]$: New Emissive Material

non-linear optics: SHG ?

→ irradiation by CW infrared laser diode

→ directed white-light emission !



N. W. Rosemann, J. P. Eußner, A. Beyer, S. W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* **2016**, *352*, 301.

$[(R^{Sty}Sn)_4S_6]$: New Emissive Material

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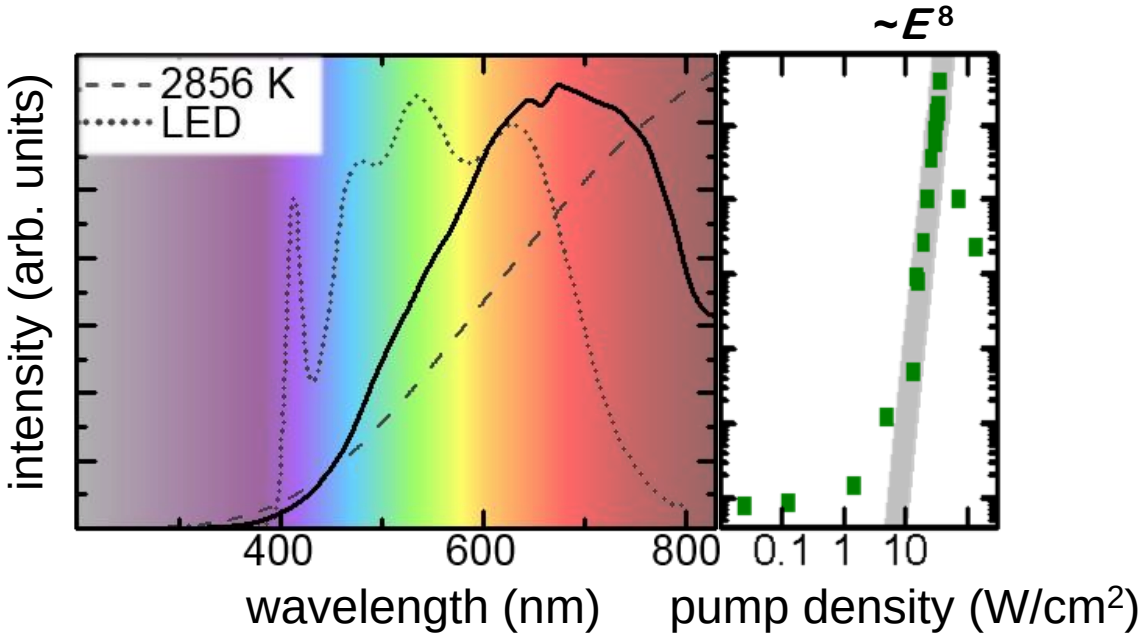

→ supercontinuum generation *without* pulsed laser

N. W. Rosemann, J. P. Eußner, A. Beyer, S. W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* **2016**, *352*, 301.

[($R^{Sty}Sn)_4S_6$]: New Emissive Material

non-linear optics: SHG ?

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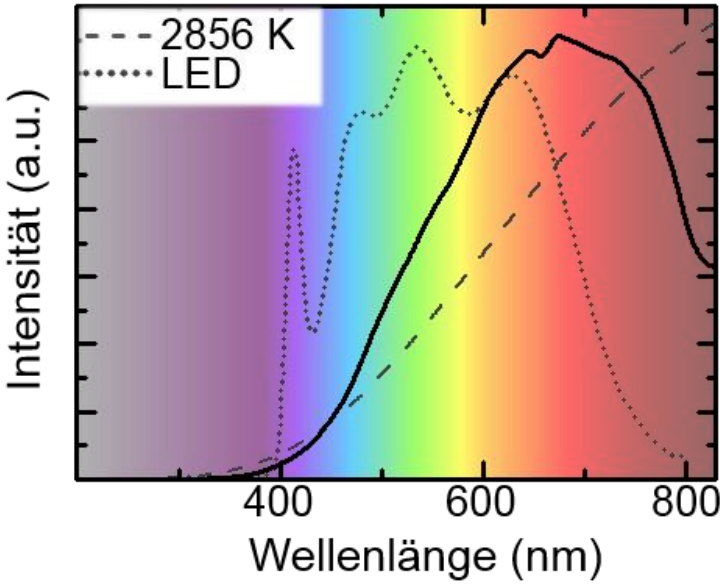


→ supercontinuum generation *without* pulsed laser

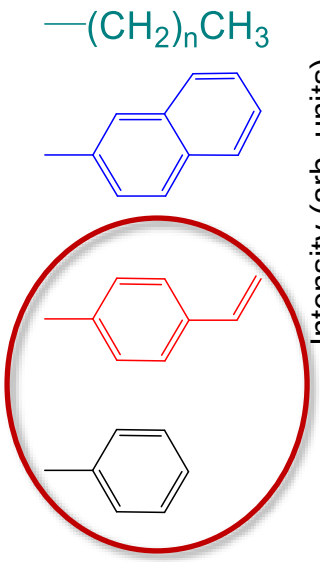
N. W. Rosemann, J. P. Eußner, A. Beyer, S. W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* **2016**, *352*, 301.

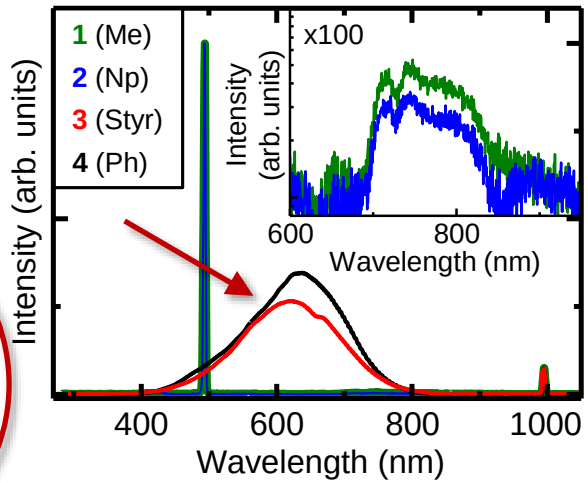
$[(RT)_4E_6]$: New Emissive Materials

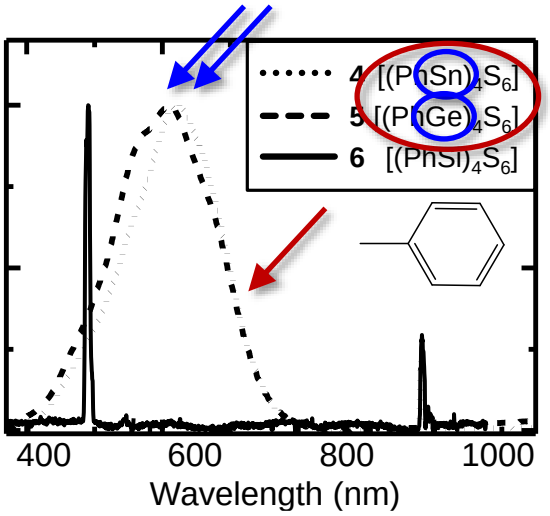
Karlsruhe Institute of Technology

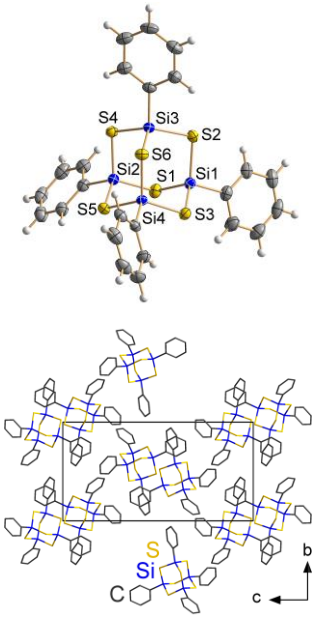
variation of R, T, E:

→ WLG *or* SHG









Me/Sn/S: Haas et al., *Chem. Ber.* **1987**, *120*, 1175.
Ph/Sn/S: Scherer et al., *Acta Crystallogr.* **1972**, *B28*, 2323.
Ph/Si/S: Lüpschen et al., *Naturforsch.* **1971**, *26b*, 1191

→ WLG: cyclic R and no long-range order

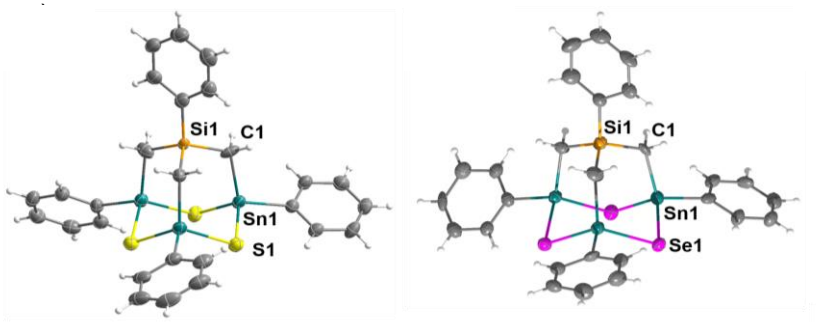
→ fine-tuning of λ_{max} by variation of T, E

K. Hanau, S. Schwan, M. R. Schäfer, M. J. Müller, C. Dues, SS, SC, DM, SD, *Angew. Chem. Int. Ed.* **2021**, *60*, 1176.
E. Dornsiepen, F. Dobener, S. Chatterjee, SD, *Angew. Chem. Int. Ed.* **2019**, *58*, 17041–17046.
N.W. Rosemann, J.P. Eußner, E. Dornsiepen, S. Chatterjee, SD, *J. Am. Chem. Soc.* **2016,** *138*, 16224−16227.

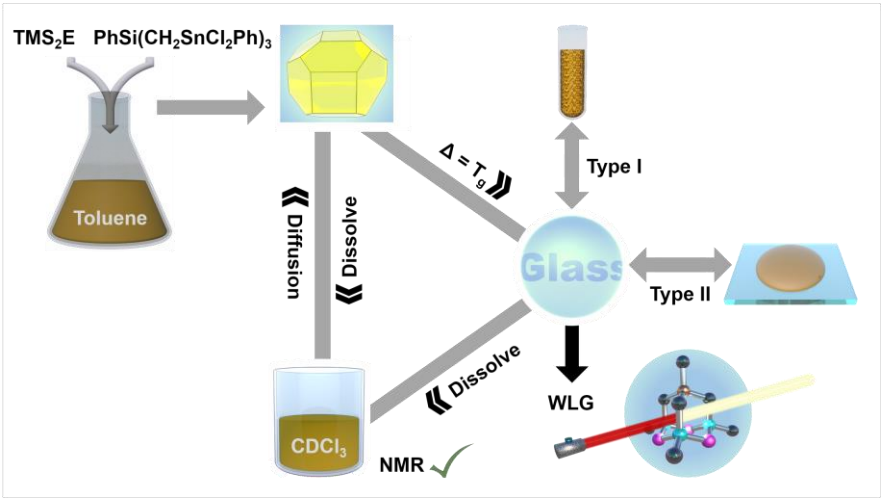
Multinary Cluster Cores ⇒ Cluster Glass

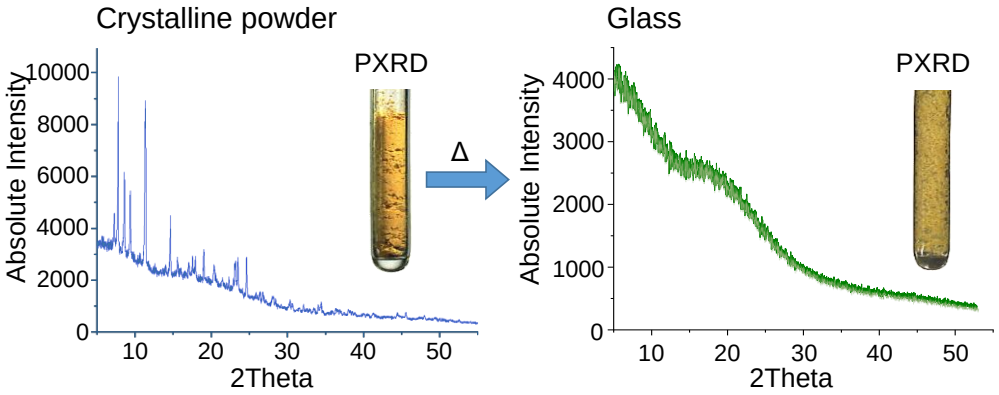
Karlsruhe Institute of Technology

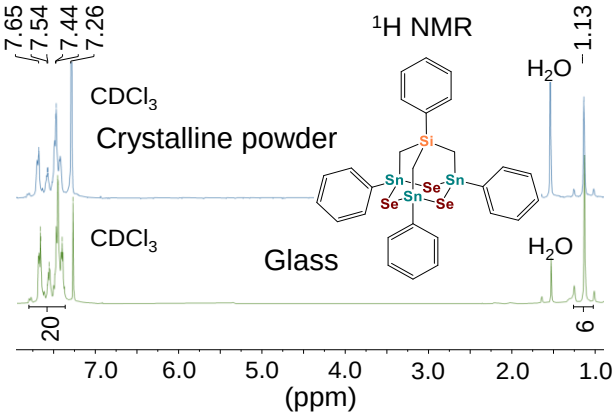
glass formation from crystals



$[(PhSi)(CH_2)_3(PhSn)_3E_3]$







→ glassy material comprising *intact* cluster molecules

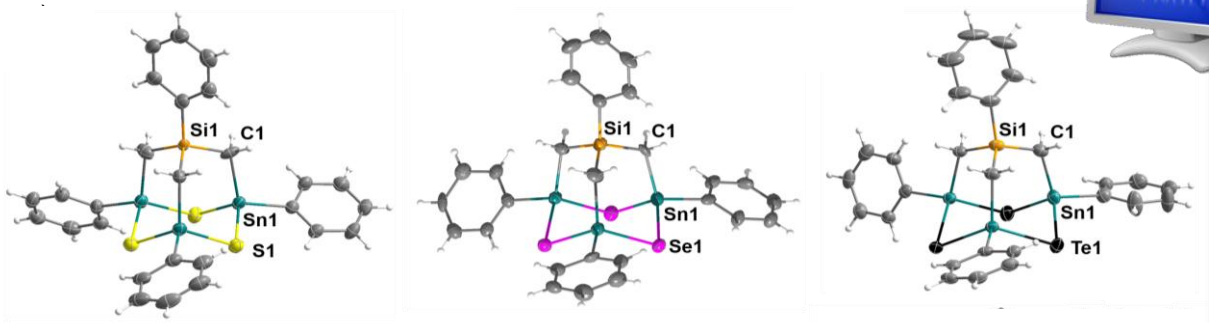
→ larger robustness and processability

I. Rojas Léon, J. Christmann, S. Schwan, F. Ziese, S. Sanna, D. Mollenhauer, NWR, SD, *Adv. Mater.* **2022**, *34*, 2203351.

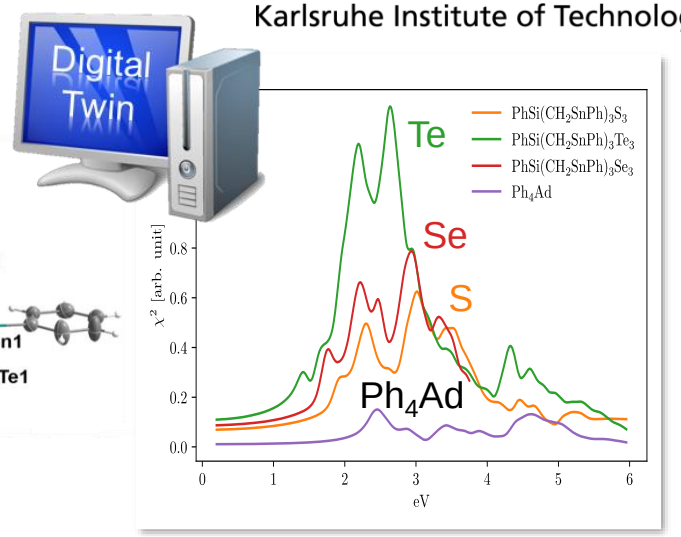
Multinary Cluster Cores ⇒ Cluster Glass

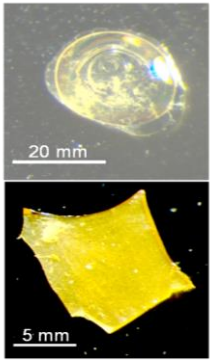
Karlsruhe Institute of Technology

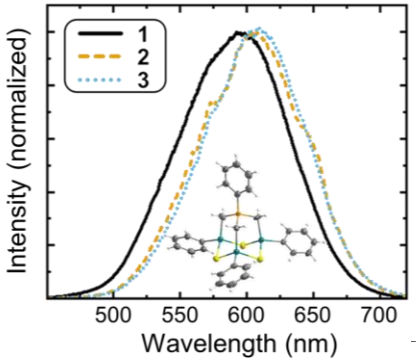
glass formation from crystals

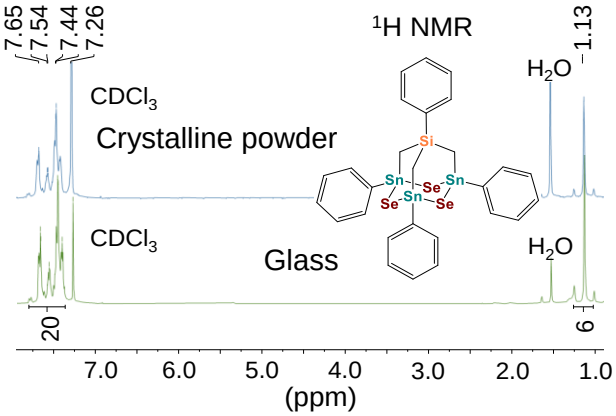


$[(PhSi)(CH_2)_3(PhSn)_3E_3]$









→ larger robustness and processability

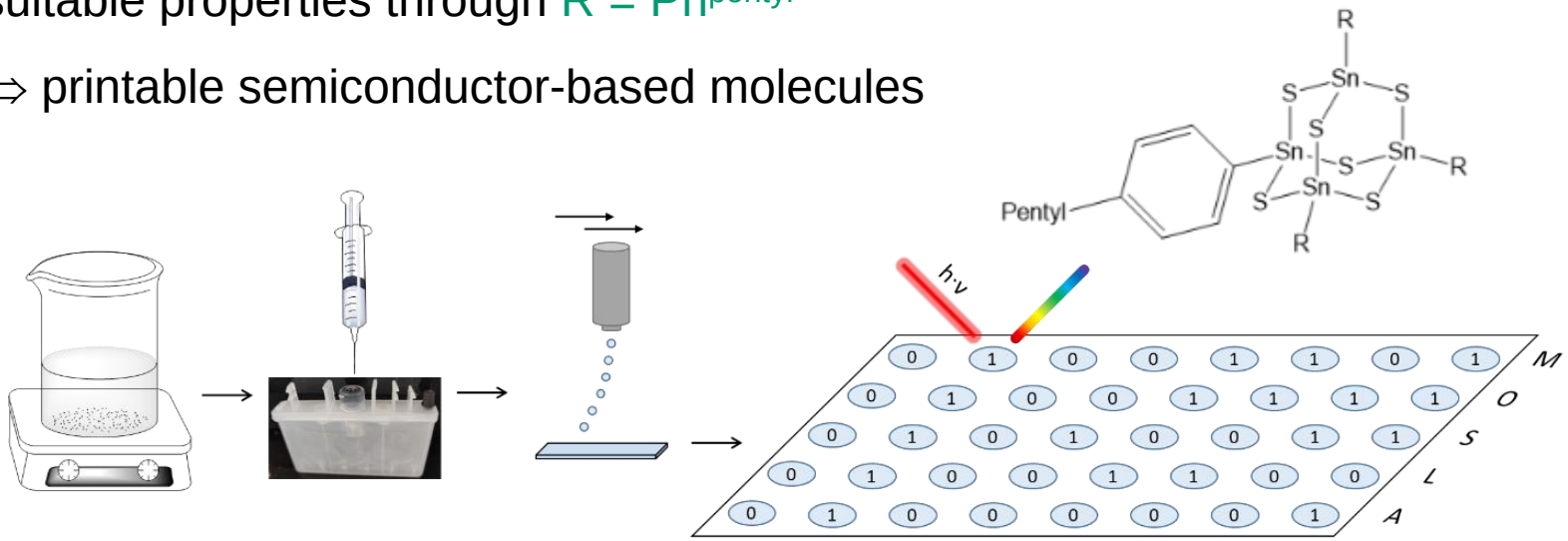
→ core heterogeneity enhances WLG intensity ⇒ basis for further design

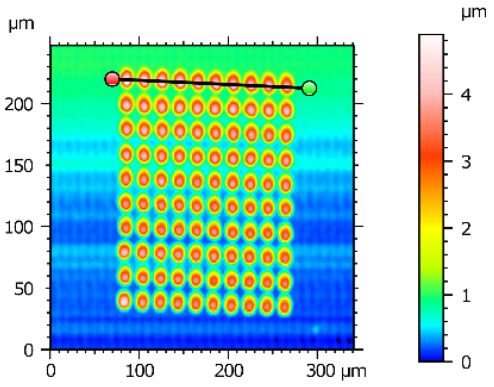
I. Rojas Léon, J. Christmann, S. Schwan, F. Ziese, S. Sanna, D. Mollenhauer, NWR, SD, *Adv. Mater.* **2022**, *34*, 2203351.

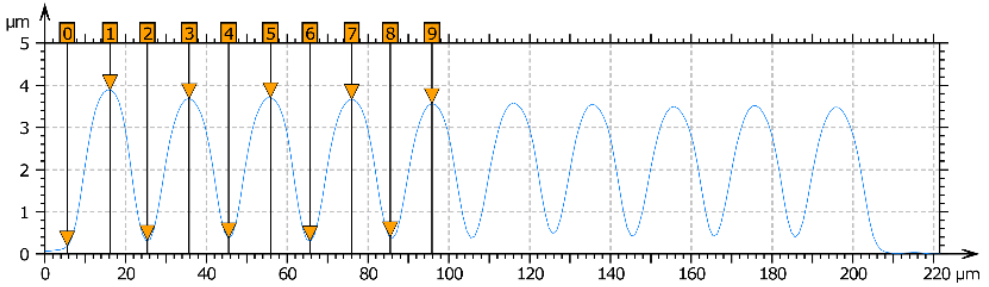
Inorganic Cluster-Based Inks

suitable properties through R = Ph^{pentyl}

⇒ printable semiconductor-based molecules







Parameters	Unit	0-1	2-3	4-5	6-7	8-9
Horizontal distance	µm	10.61	10.32	10.32	10.32	10.32
Height difference	µm	3.699	3.360	3.327	3.358	3.159

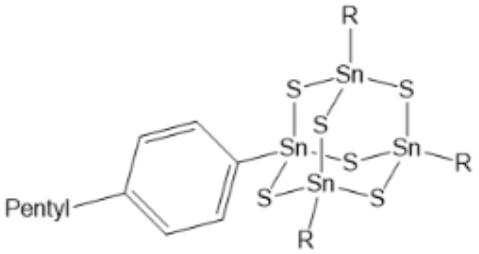
→ laterally regular pattern with equal height profile

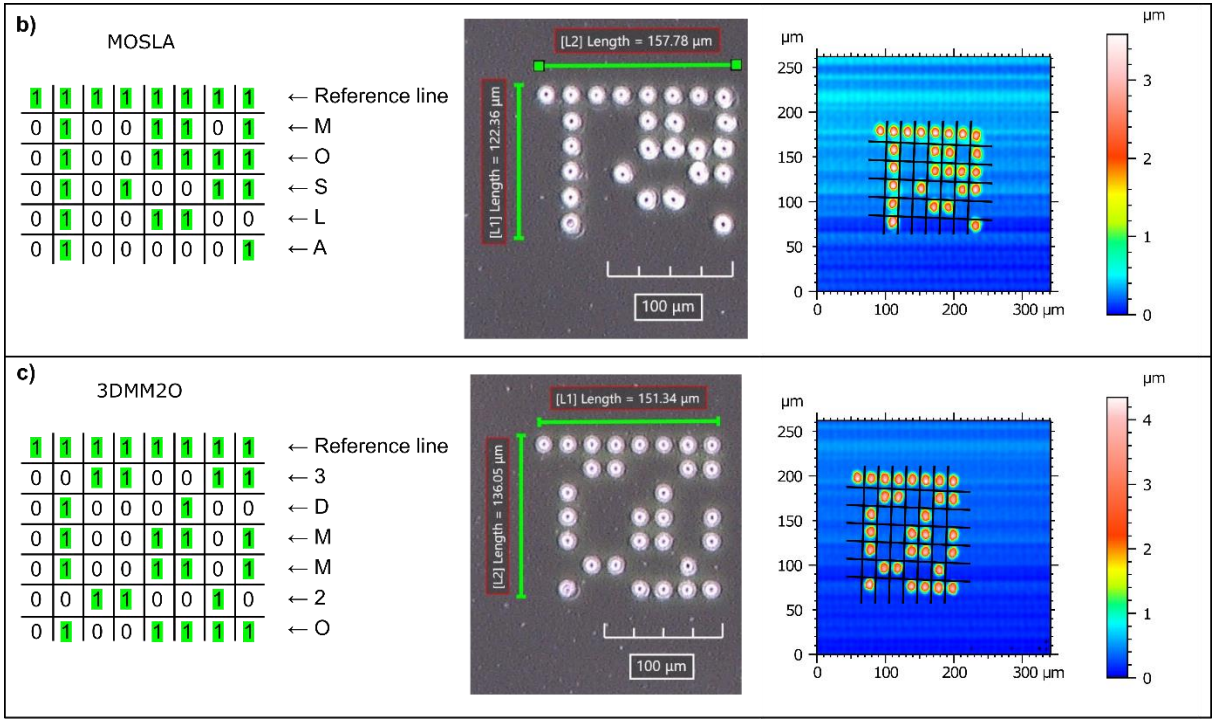
S. Nier, E. Dörsam, J. Aghassi-Hagmann, SD, **2023**, *in preparation*.

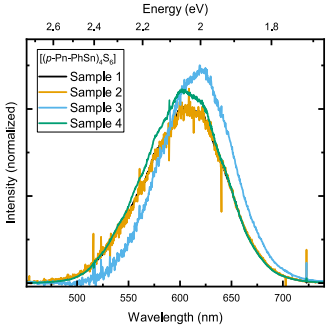
Inorganic Cluster-Based Inks

suitable properties through R = Ph^{pentyl}

⇒ printable semiconductor-based molecules







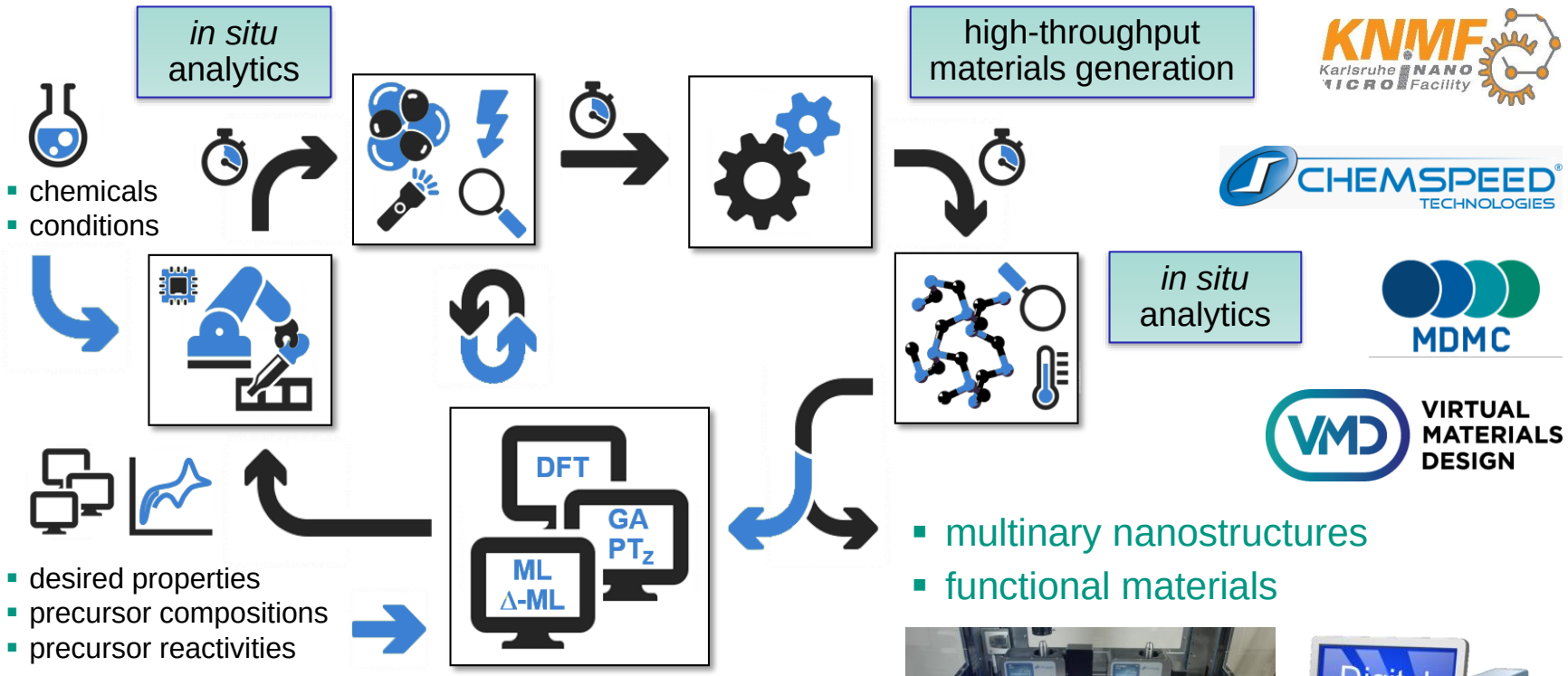
→ binary code using white-light emissive material

S. Nier, E. Dörsam, J. Aghassi-Hagmann, SD, **2023**, *in preparation*.

Perspective: Accelerated Development

Karlsruhe Institute of Technology

materials acceleration platform: Auto.MAP @ KIT



combination with additive manufacturing

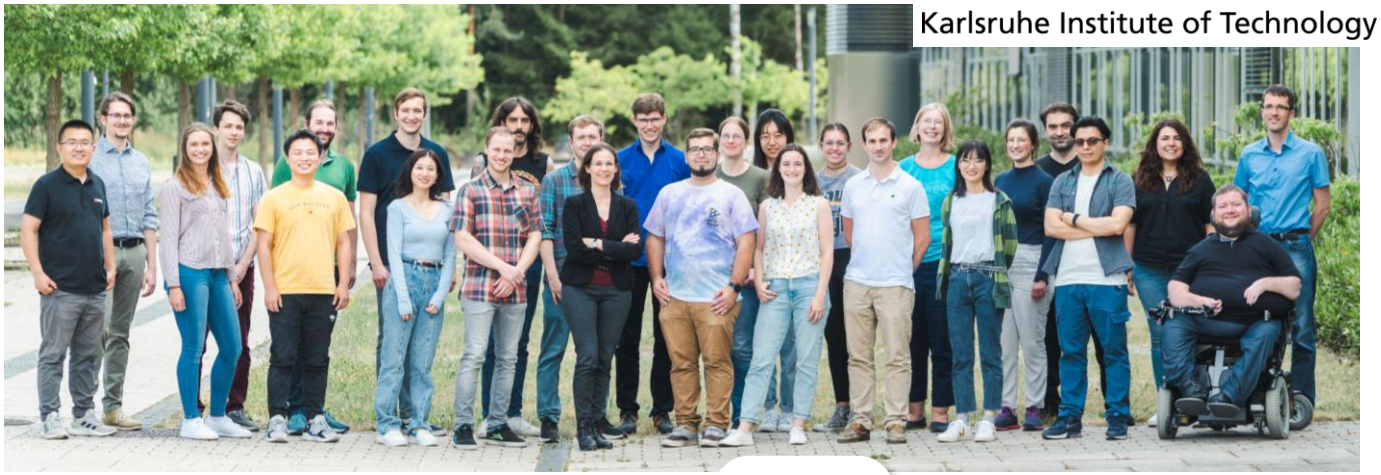
⇒ automated and autonomous approach to multinary cluster-based materials

Credit Goes To…

Karlsruhe Institute of Technology

Current Group

M. Ahmadi
K. Beuthert
J. Christmann
M. Diels
K. Flosdorf
Dr. G. Gomez
Dr. L. Guggolz
Dr. S. Klementyeva
Y. Lohse
S. Nier
Dr. F. Pan
Dr. B. Peerless
Dr. A. Pankajakshan
L. Redpath
J. Rienmüller
Dr. N. Rinn
Dr. I. Rojas Leon
A. Schmidt
N. Spang
G. Stuhrmann
M. Szabo
A. Tschirch
J. Wang
Dr. Y. Wang
S. Wei
Dr. B. Weinert
Z. Wu



and…

Collaborations

F. Weigend, Y. F. Franzke, W. Massa, R. Clérac, R. Dronskowski, K. Volz, B. Roling, S. Chatterjee, S. Sanna, W.-C. Pilgrim, D. Mollenhauer, F. Kraus, D. Sundholm M. Gottfried, S. Adams, B. Kirchner, P. W. Roesky, T. Vitova, C. Feldmann, M. Koch

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erc BiCMat
3D MATTER MADE TO ORDER
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FOR 2824
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Former PhD students and Postdocs

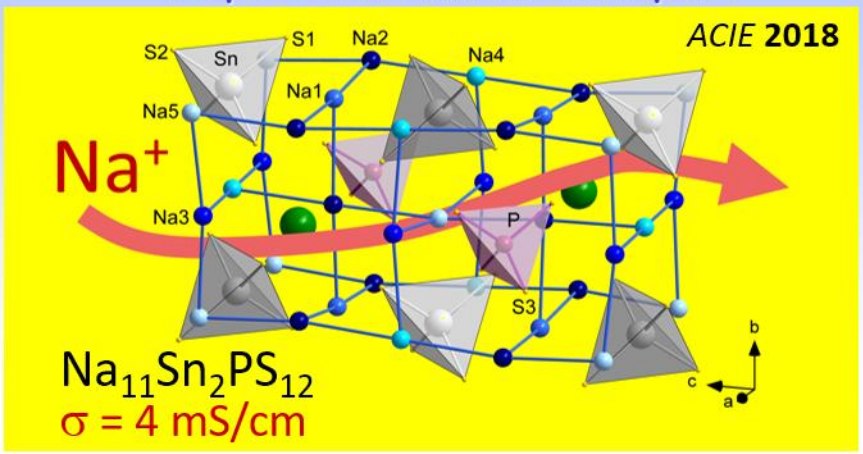
Dr. R. Ababei, Dr. B. Barth,
Dr. L. Broeckaert, Dr. P. Bron,
Dr. C. Donsbach, Dr. E. Dornsiepen,
Dr. A. Engel, Dr. A. Eulenstein,
Dr. J. Eußner, Dr. E. Geringer,
Dr. S. Haddadpour, Dr. R. Halvagar,
Dr. Z. Hassanzadeh, Dr. S. Heimann,
Dr. C. Hosier, Dr. T. Kaib,
Dr. E. Leusmann, Dr. Z. Lin,
Dr. F. Lips, Dr. N. Lichtenberger,
Dr. Y. Lin, Dr. M. Melullis,
Dr. S. Mitzinger, Dr. S. Nayak,
Dr. H. P. Nayek, Dr. H. Niedermeyer,
Dr. C. Pöhlker, Dr. B. Peters,
Dr. M. Reinmuth, Dr. E. Ruzin,
Dr. S. Santner, Dr. G. Thiele,
Dr. R. J. Wilson, Dr. W. Yu,
Dr. Z. You, Dr. C. Zimmermann

JACS **2013**; *J. Power Sources* **2016**, **2017**; *ACIE* **2018**

JACS **2023**; *JACS Au* **2022**, *ACIE* **2021**; *Chem. Sci.* **2019**, **2020**

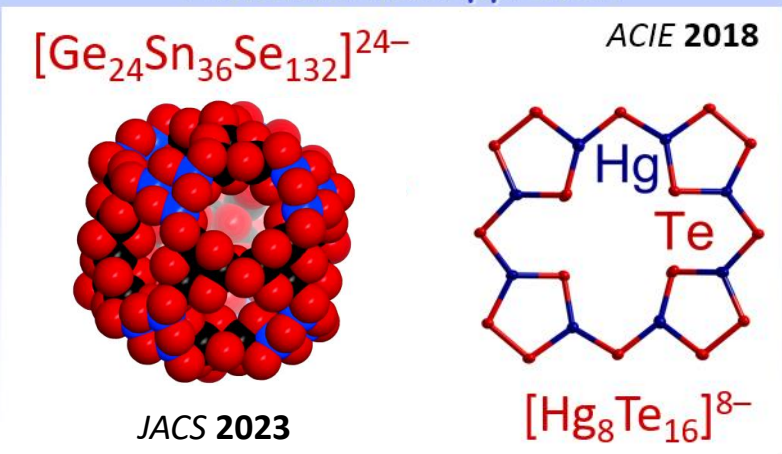
Multinary Chalcogenidometalates

→ Opto-Electronics & Transport

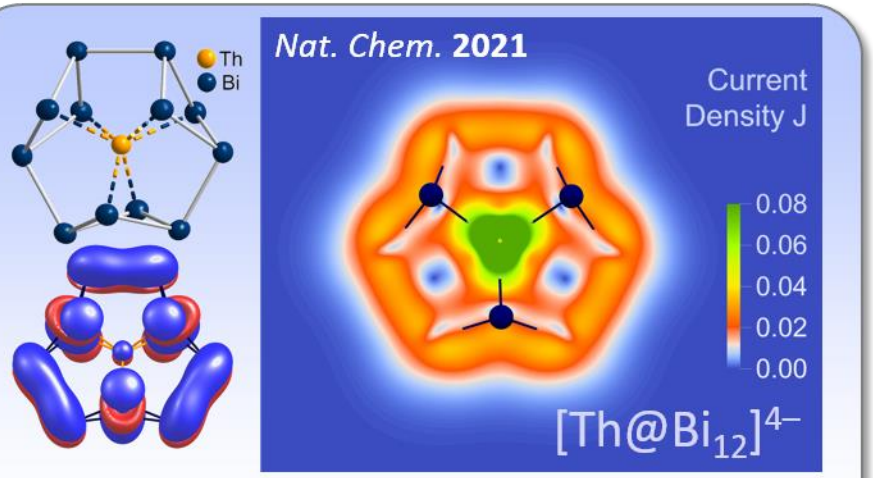


Non-Classical Chalcogenidometalates

→ Ionothermal Approach



Multinary Clusters as Basis for Uncommon Materials



Zintl Clusters and Polyanions

→ Formation Pathways, Bonding & Reactivity

Organyl Functionalized Cages & Networks

→ Multifunctionality & Molecular Containment

Nat. Chem. **2023**, **2021**; *Nat. Comm.* **2021**; *ACIE* **2023**; *JACS* **2021**

Science **2016**; *JACS* **2019**; *ACIE* **2021**; *Adv. Mater.* **2022**

Karlsruhe Institute of Technology

Multinary Clusters as Basis for Uncommon Materials

Stefanie Dehnen
Institute of Nanotechnology

Helmholtz-Zentrum hereon

MSE Day
Geesthacht, Nov 14, 2023