Bis((dialkylamino)alkylselenolato)-metalcomplexes as precursors in the syntheses of metal selenide nanoparticles in [BMIm][BF_4]

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Metal chalcogenides

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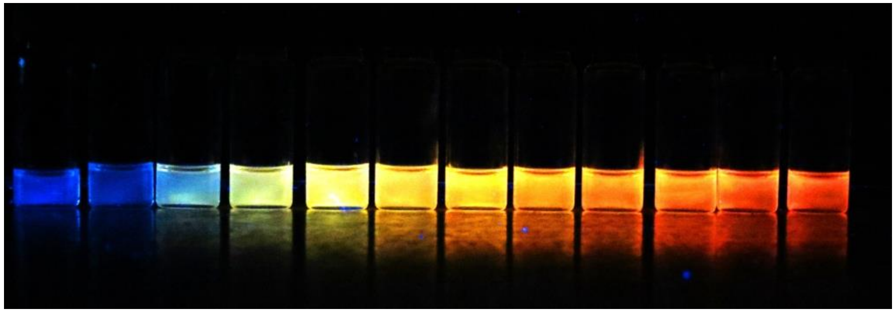
- **Various properties and aplications**
  - Semiconductivity[1,2,3,4]
  - Nonlinear optical properties [2]
  - Superconductivity
  - Electron tunneling[2]
  - Thermoelectrically properties
  - Catalytic activity
  - Solar cells[1,3]
  - Detector materials[3]
  - Photo resistors[3]
  - Telecommunication devices[3,4]
  - Switching elements
  - Bioengineering[4]

[1] Matthew L., *J. Chem. Ed.,* 2014, **91**, 274−279

[2] Sugimoto T.; *Elsevier*, Amsterdam, London, New York, 2001, 792

[3] J. Akhtar, J. C. Bruce et. al., *Mater. Res. Soc. Symp. Proc.* 2009, 1148-PP12-08

[4] N. Moloto, *Dissertation* , 2010**,** University of the Witwatersrand



Semiconductor nanocrystals

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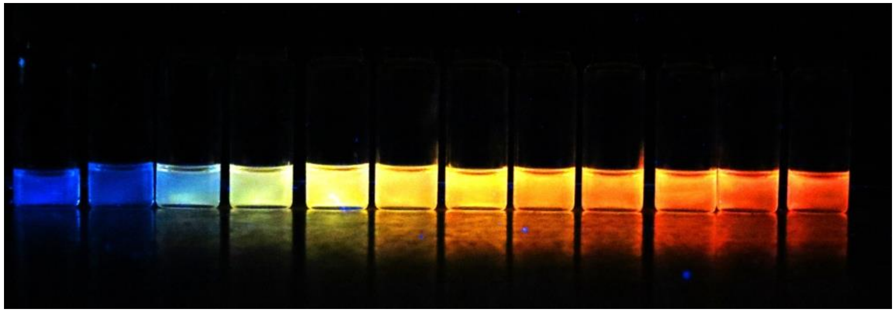
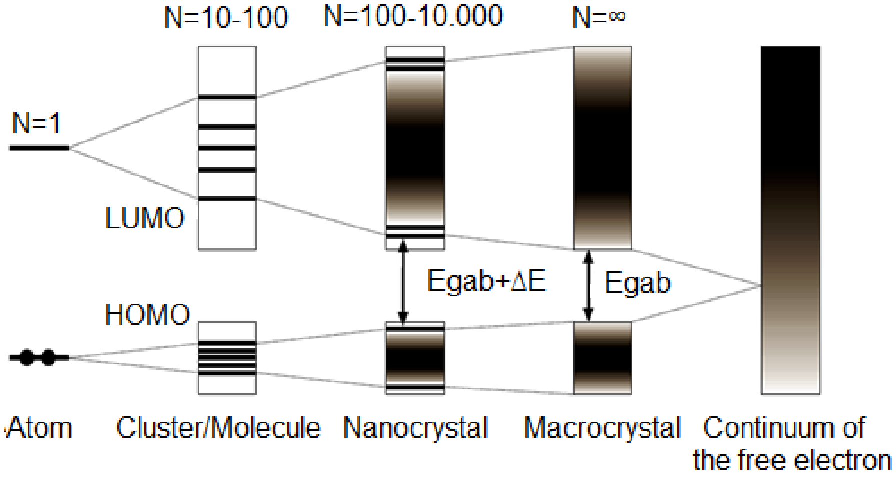
- Novel properties (electron tunneling, size quantization of energy levels [1,2]), result in applications in various fields (telecommunication systems, optoelectronics, IR detectors, solar cells, photorisistors [3], catalysis and bioengineering)
- Discretization of the electronic energy levels beneath 7.6 nm (particle in the box)
- Hypsochromic shift of the absorption due to quantum confinement





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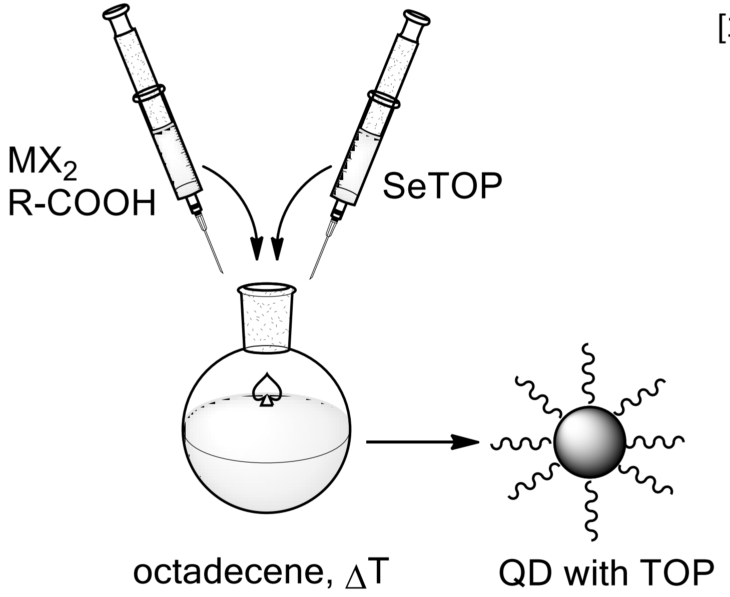
[2] Sugimoto T.; *Elsevier*, Amsterdam, London, New York, 2001, 792

[3] J. Akhtar, J. C. Bruce et. al., *Mater. Res. Soc. Symp. Proc.* 2009, 1148-PP12-08

Hot Injection Method [1]

- In the classical synthesis metal chalcogenide quantum dots are produced by simultaneously injecting metal and selenium precursor solutions into a heated growth solution of octadecene
- The particle size can be varied by the reaction time and the temperature
- Usually these particles are stabilized by stabilizing agents such as hexadecylamine (HDA) or trioctylphosphine (TOP)

[1]



[1] Matthew L., *J. Chem. Ed.*, 2014, **91**, 274−279

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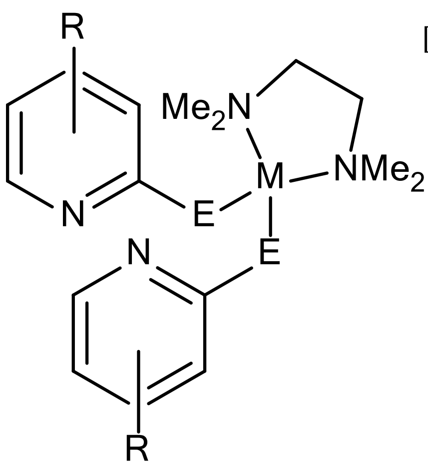
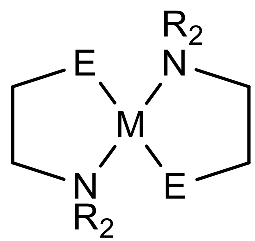
Single source precursors for metal chalcogenide nanoparticles

[6]





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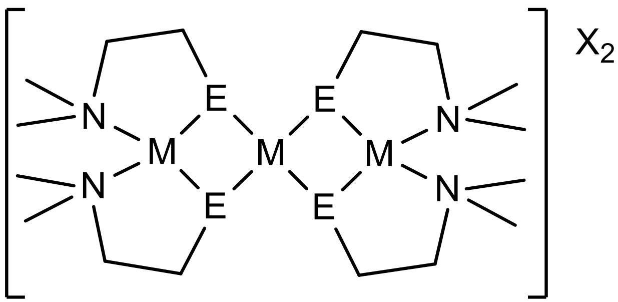

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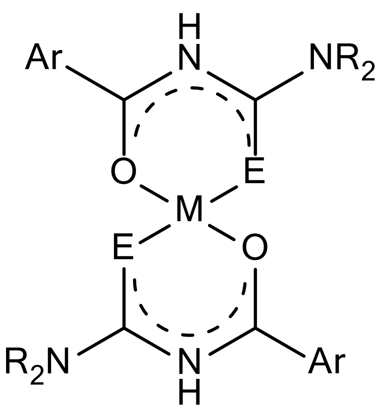

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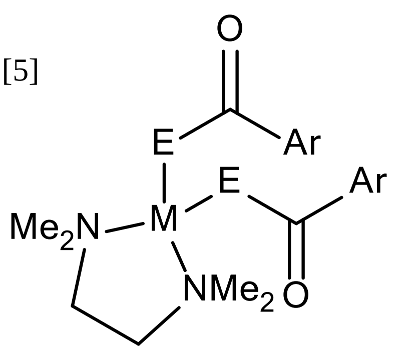


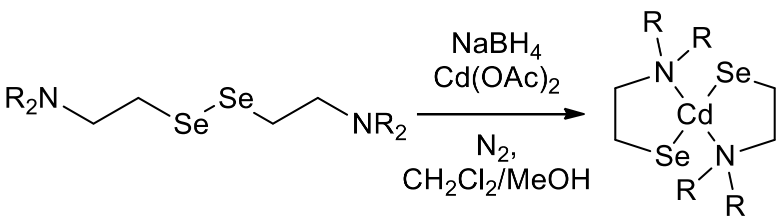
[5] V. K. Jain *et al.*, *Dalton Trans.*, 2006, 2714–2718

[6] V. K. Jain *et al.*, *Inorg. Chim. Ac.* 2011, **365,** 333–339

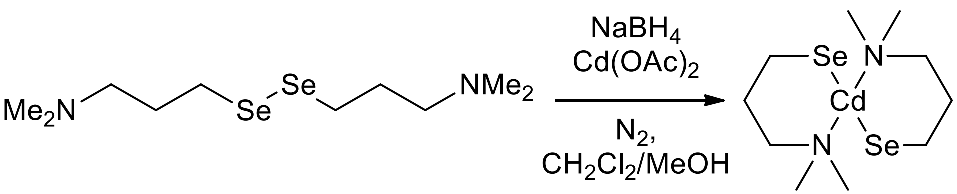
[7] V. K. Jain *et al.*; *Polyhedron* 2006, **25**, 2383–2391

[8] J. Akhtar, P. O`Brien *et al*, *Eur. J. Inorg. Chem.* 2011, 2984–2990

CdSe NPs in [BMIm][BF_4]



R = Me **(1)** or Et **(2)**



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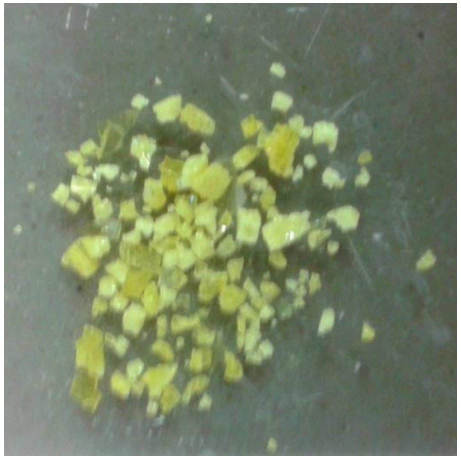
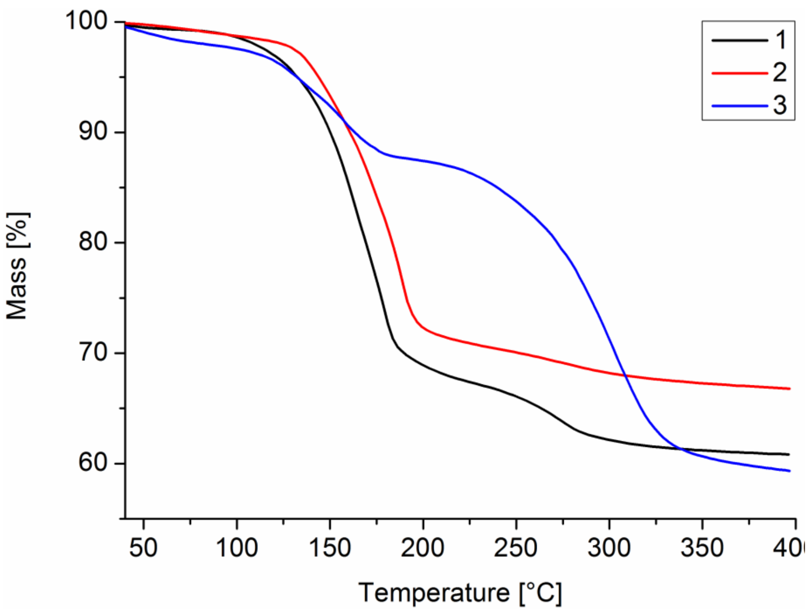




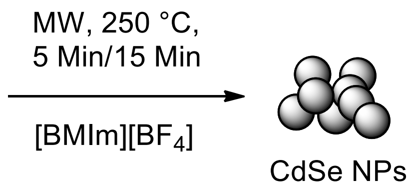
Precursor	Yield [%]	Δm [%]	$\Delta m_{theor.}$ [%]	Decomp. temp. [°C]	CdSe crystal system[a]
1	61	38	35	150	hexagonal $P6_3mc$
2	42	39	39	165	hexagonal $P6_3mc$
3	18	39	39	155	hexagonal $P6_3mc$

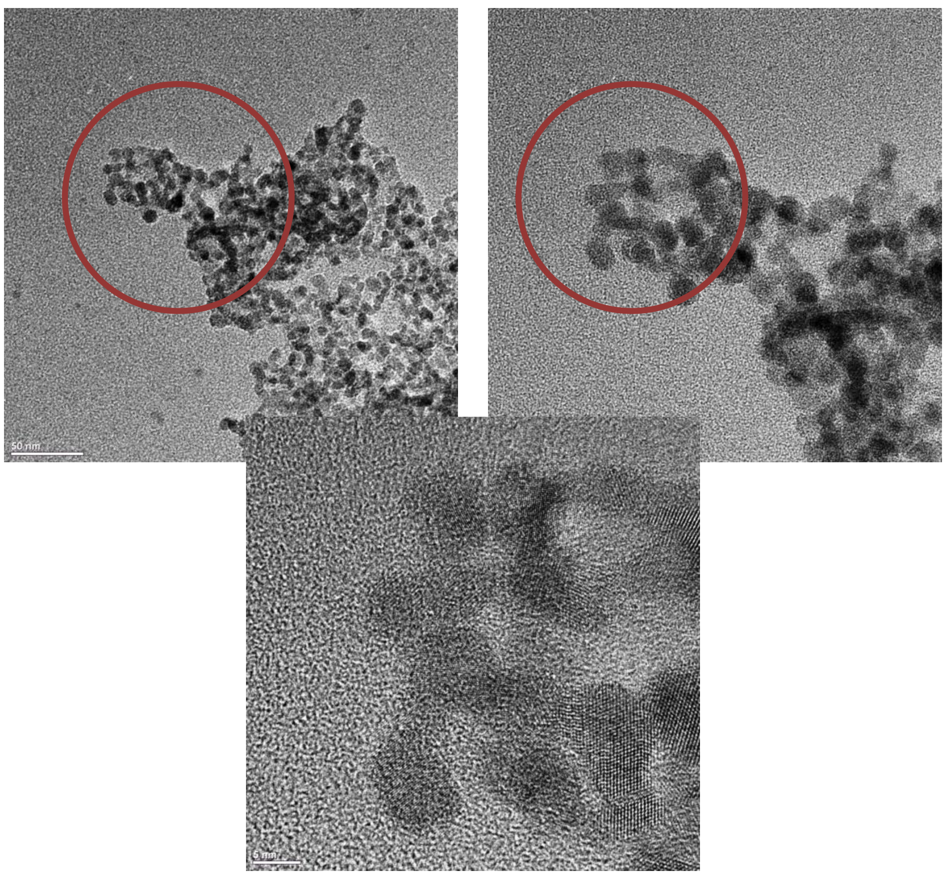
[a] From PXRD analysis of the residue of the thermal analysis (hexagonal CdSe, reference: COD- database: 9008863).

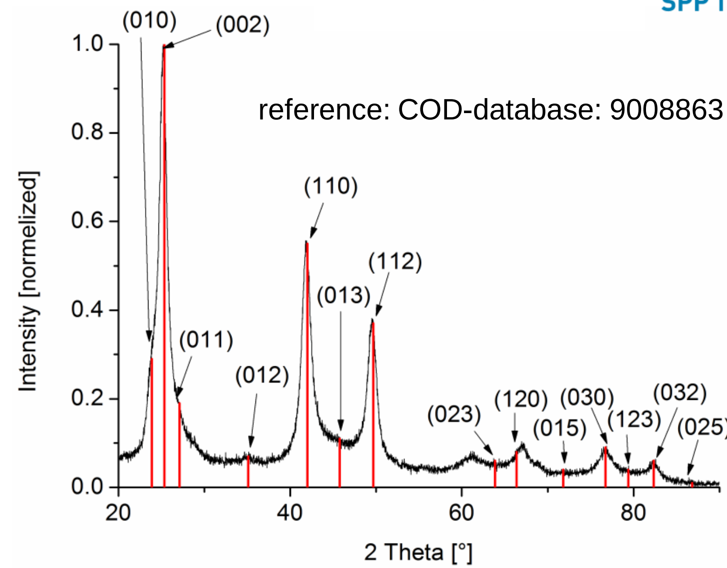
[7] V. K. Jain *et al.*; *Polyhedron* 2006, **25**, 2383–2391

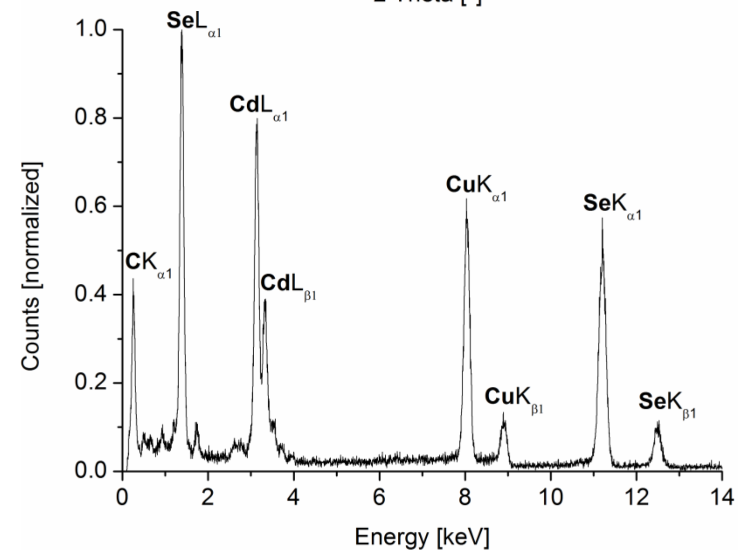
CdSe NPs in in [BMIm][BF_4]

[Cd($Me_2NEtSe)_2$] **(1)**
[Cd($Et_2NEtSe)_2$] **(2)**
[Cd($Me_2NPrSe)_2$] **(3)**









CdSe NPs in in [BMIm][BF_4]

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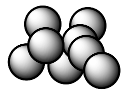
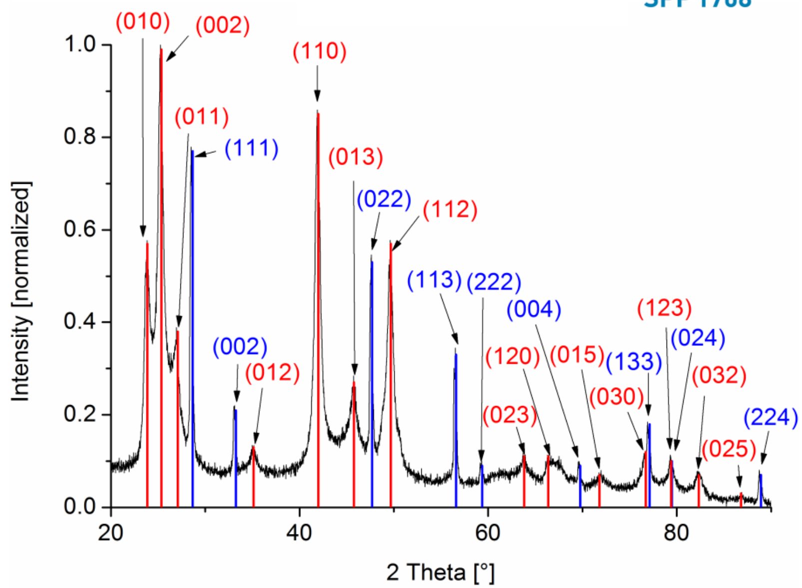
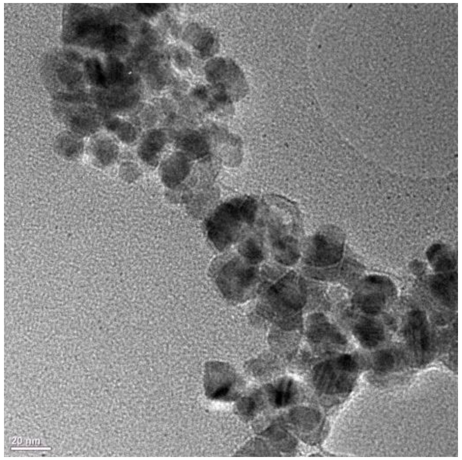
$Cd(OAc)_2$ + Diselenide → (MW, 250 °C, 15 Min; [BMIm][BF_4]) CdSe NPs



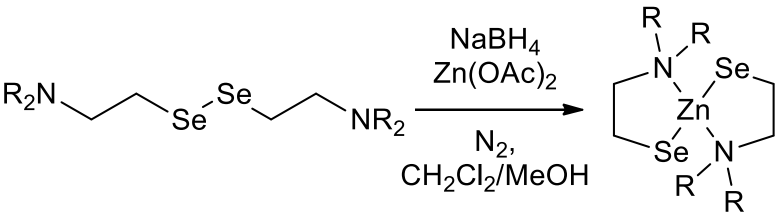
Precursor	NPs	Ø-NPs TEM [nm]	Ø-NPs PXRD [nm]	crystal system
1 (5min)	CdSe	20.0 ± 2.9	10.5 ± 1.3	hexagonal ($P6_3mc$)
2 (5min)	CdSe	11.9 ± 2.5	8.0 ± 0.8	hexagonal ($P6_3mc$)
3 (5min)	CdSe	9.3 ± 1.3	7.9 ± 0.7	hexagonal ($P6_3mc$)
1 (15min)	CdSe	27.3 ± 3.5	8.0 ± 1.8	hexagonal ($P6_3mc$)
2 (15 min)	CdSe	18.6 ± 2.9	9.6 ± 1.3	hexagonal ($P6_3mc$)
3 (15 min)	CdSe	10.9 ± 1.7	7.8 ± 0.5	hexagonal ($P6_3mc$)
$Cd(OAc)_2$ +	CdSe +	-	22.9 ± 3.2	hexagonal ($P6_3mc$)
$(Me_2NEtSe)_2$	CdF_2		38.6 ± 4.8	cubic (Fm-3m)
$Cd(OAc)_2$ +	CdSe +	18.3 ± 2.5	22.5 ± 2.9	hexagonal ($P6_3mc$)
$(Et_2NEtSe)_2$	CdF_2		38.6 ± 4.8	cubic (Fm-3m)
$Cd(OAc)_2$ +	CdSe +	19.1 ± 2.3	13.5 ± 0.6	hexagonal ($P6_3mc$)
$(Me_2NPrSe)_2$	CdF_2		30.5 ± 1.7	cubic (Fm-3m)



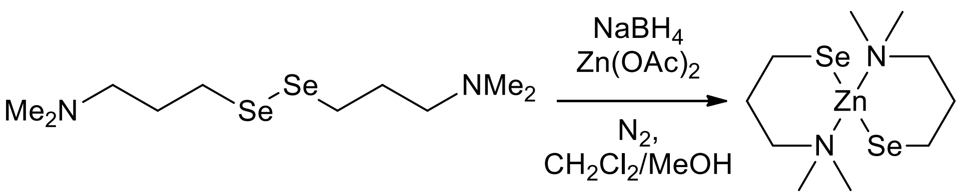
reference: COD-database: 9008863 (CdSe), 9009006 (CdF_2)



ZnSe NPs in [BMIm][BF_4]



R = Me **(4)** or Et **(5)**



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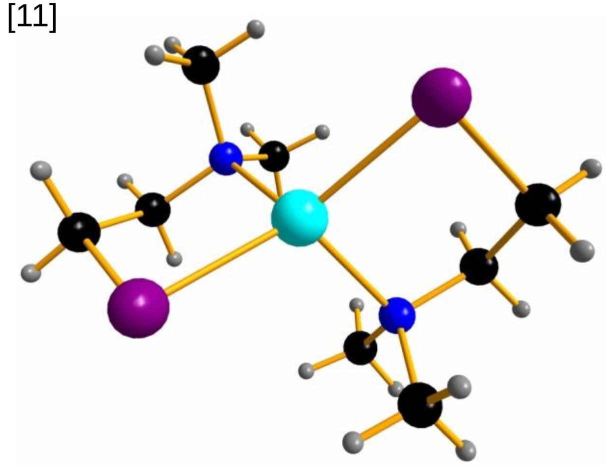
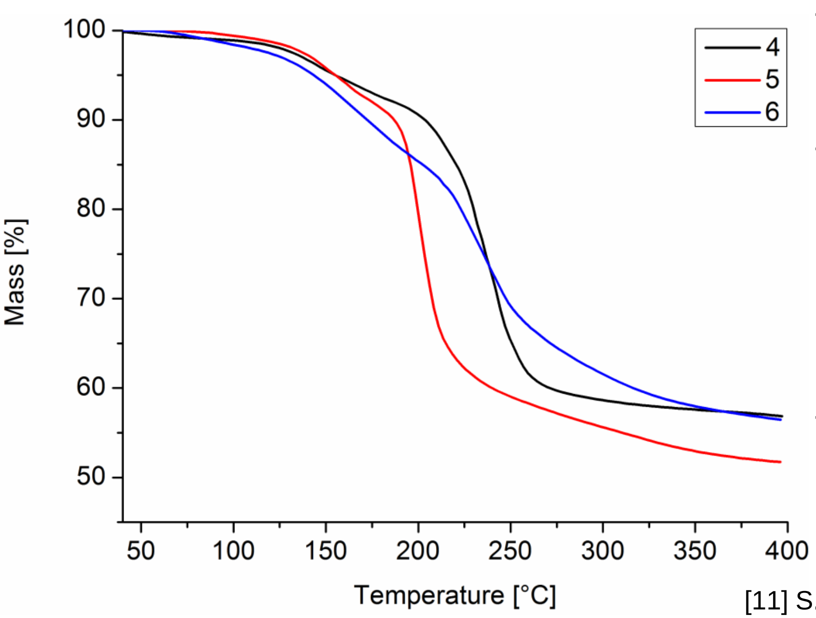




Precursor	Yield [%]	Δm [%]	$\Delta m_{theor.}$ [%]	Decomp. temp. [°C]	ZnSe crystal system[a]
4	78	43	39	220	hexagonal $P6_3mc$
5	35	48	45	210	hexagonal $P6_3mc$
6	67	43	43	215	cubic F-43m

[a] From PXRD analysis of the residue of the thermal analysis (hexagonal ZnSe, reference: COD- database: 9008879; cubic ZnSe, reference: COD-database: 9008857

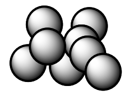
[11] S. Dey, V. K. Jain, S. Chaudhury, A. Knoedler and W. Kaim, *Polyhedron, 2003,* ***22,*** 489

ZnSe NPs in in [BMIm][BF_4]

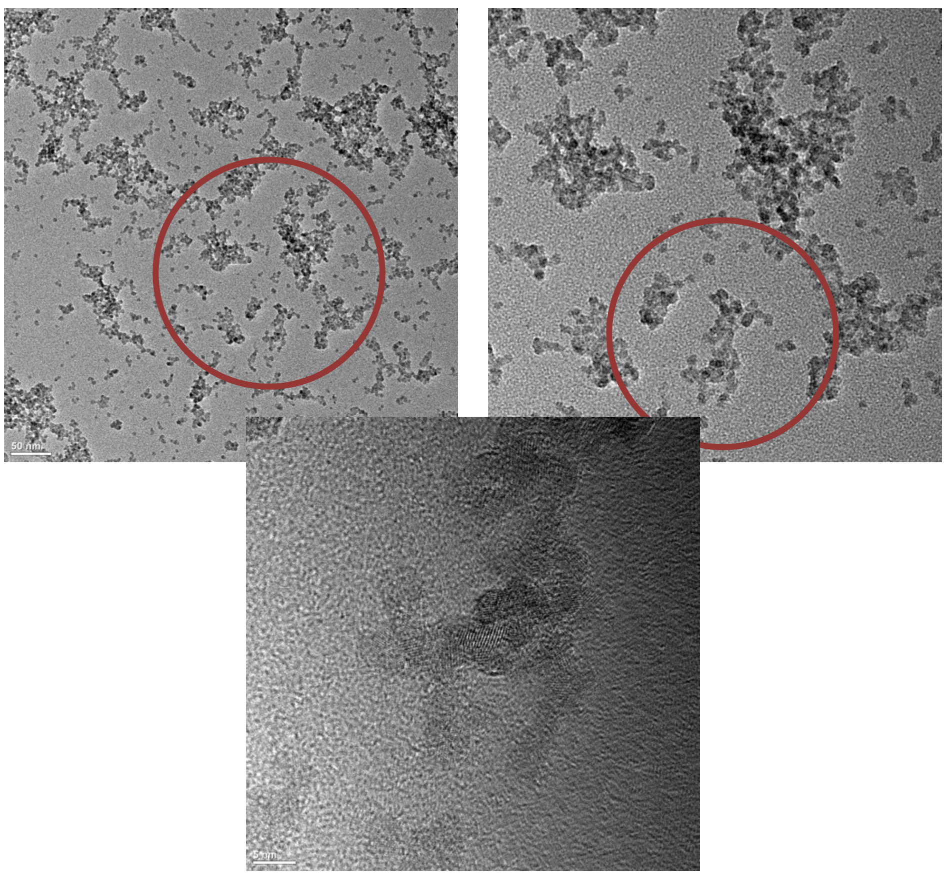
$[Zn(Me_2NEtSe)_2]$ **(4)**
$[Zn(Et_2NEtSe)_2]$ **(5)**
$[Zn(Me_2NPrSe)_2]$ **(6)**

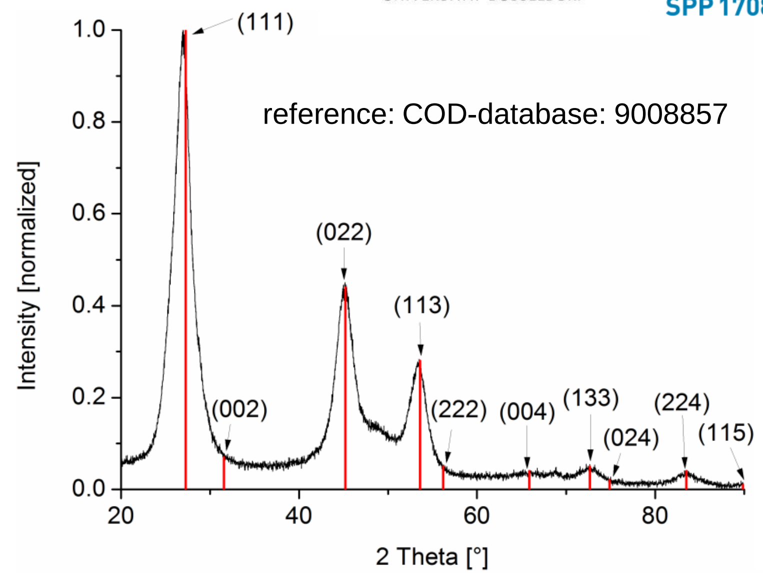
MW, 250 °C,
5 Min/15 Min

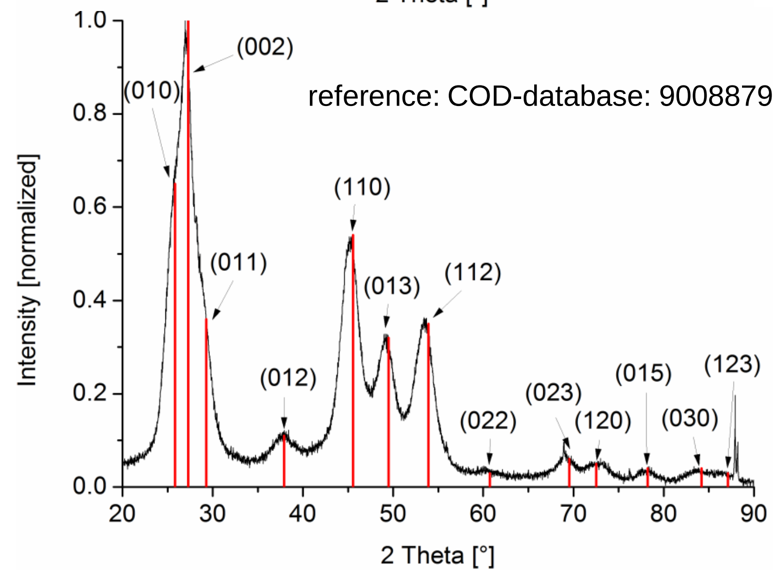
[BMIm][BF_4]



ZnSe NPs

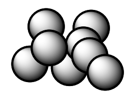




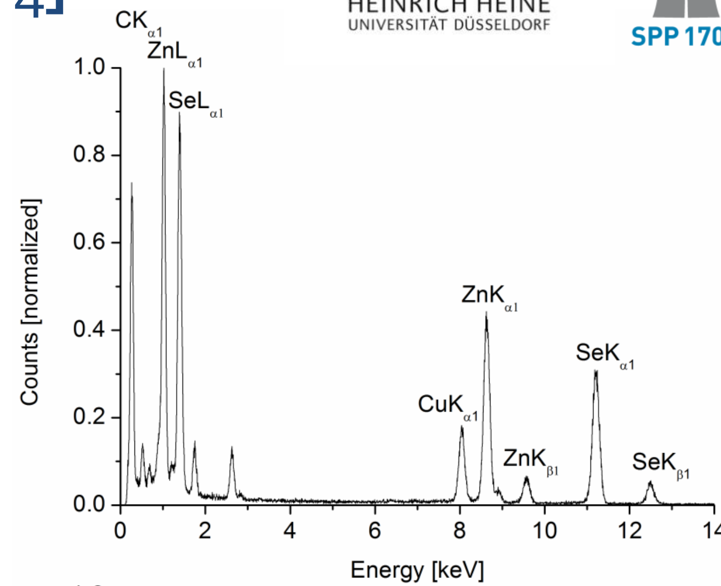


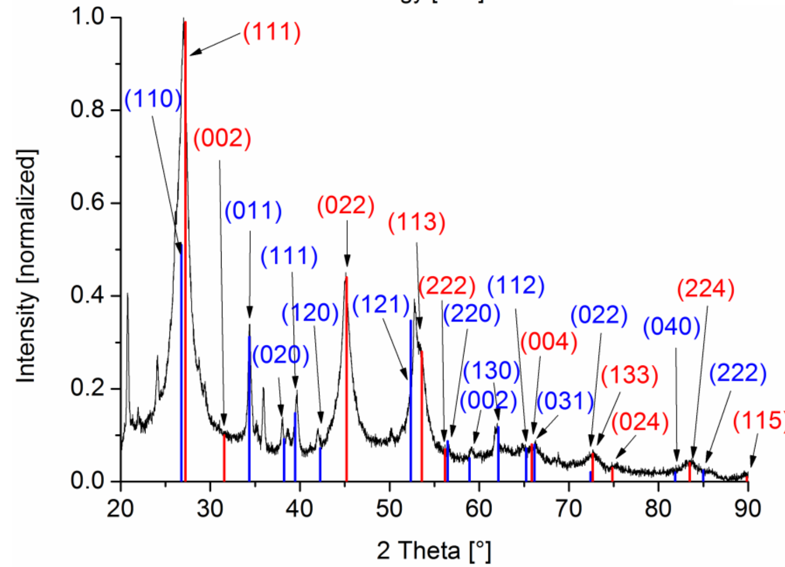
ZnSe NPs in in [BMIm][BF_4]

$Zn(OAc)_2$ + Diselenide → (MW, 250 °C, 15 Min; [BMIm][BF_4]) → ZnSe NPs



Precursor	NPs	Ø-NPs TEM [nm]	Ø-NPs PXRD [nm]	crystal system
4 (5min)	ZnSe	7.0 ± 1.9	4.0 ± 0.8	hexagonal ($P6_3mc$)
5 (5min)	ZnSe	4.7 ± 1.3	4.3 ± 0.4	cubic (F-43m)
6 (5min)	ZnSe	4.0 ± 0.9	4.3 ± 0.5	cubic (F-43m)
4 (15min)	ZnSe	5.0 ± 2.3	4.2 ± 0.4	cubic (F-43m)
5 (15 min)	ZnSe	4.4 ± 1.1	4.8 ± 1.0	cubic (F-43m)
6 (15 min)	ZnSe	4,7 ± 2.1	4.5 ± 0.7	cubic (F-43m)
$Zn(OAc)_2$ + $(Me_2NEtSe)_2$	ZnSe	-	6.2 ± 0.8	cubic (F-43m)
$Zn(OAc)_2$ + $(Et_2NEtSe)_2$	ZnSe + ZnF_2	-	5.8 ± 1.9 13.2 ± 0.8	cubic (F-43m) cubic (Fm-3m)
$Zn(OAc)_2$ + $(Me_2NPrSe)_2$	ZnSe	-	5.4 ± 0.5	cubic (F-43m)





reference: COD-database: 9008857 (ZnSe) , 2103615(ZnF_2)

Conclusions and Outlook

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Conclusions:

- Hexagonal CdSe NPs (10 – 27 nm)
- Hexagonal and cubic ZnSe NPs (4 – 5 nm)
- No further stabilizationing agents necessary
- Minor role of the ligandsystem and different decomposition times

Outlook:

- Synthesis of CdTe, ZnTe, $CdZnSe_2$, CdZnSeTe, and $CdZnTe_2$ in [BMIm][BF_4] and immobilization on TRGO
- Synthesis of other Semeiconductor-NPs in ioniq liquids and
- Optical and electronic measurements of the synthesized particles

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Thanks to:

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