# **Supporting Information**

# Analyzing and Tuning the Chalcogen-Amine-Thiol Complexes for Tailoring of Chalcogenide Syntheses

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## **Selenium Dissolution in Monoamine vs Diamine Solutions:**



Figure S1: Raman spectra of metallic Se powder used for all the solution preparation

Structure	Raman frequency (cm <sup>-1</sup> )	Assignment
Trigonal	233	Е
	237	A1
	273	2E
Orthorhombic	239	E3
	249	A1
	254	E2
Amorphous	235	Polymeric chain (A1, E)
	250	Se <sub>8</sub> (A1, E2)
Cyclic	279	Se <sub>5</sub> (A1)
	247	Se <sub>6</sub> (A1)
	285	Se <sub>7</sub> (A1)
	249	Se <sub>8</sub> (A1)
	264	Se <sub>9</sub> (A1)
	266	Se <sub>10</sub> (A1)
	258	Se <sub>12</sub> (A1)

Table S1: Selected Raman band assignments for different Se structures

#### NMR analysis of Se-BA-ET and Se-EN-ET solutions:

<sup>1</sup>H-NMR spectra were collected on a Brucker AV-III-400-HD instrument at 400 MHz frequency using  $CD_3CN$  as the solvent. Since the addition of amines to thiols lead to proton transfer reactions, the actual species present in solution are alkyl ammonium ions and thiolate ions. The byproduct of Se dissolution, dialkyl disulfides, were also confimred from NMR analysis. Structures of all proton containing species are shown below with each distinct proton labeled separately. These labeles are then used to assign corresponding peaks in <sup>1</sup>H-NMR spectra.



Figure S2: <sup>1</sup>H-NMR of Se-BA-ET solution with protons labeled according to struces presented above. (Peak at  $\delta$  of 4.45 ppm corresponds the ethylene carbonate used as NMR standard)



Figure S3: <sup>1</sup>H-NMR of Se-EN-ET solution with protons labeled according to struces presented above. (Peak at  $\delta$  of 4.45 ppm corresponds the ethylene carbonate used as NMR standard)



Figure S4: (a) the K-edge XANES spectra and (b,c) the imaginary component of the Fourier transforms (FTs) of Se K-edge k2-weighted EXAFS spectra for Se dissolved in BA-ET and EN-ET solutions with 1:1 (v/v) amine:thiol used for dissolution

#### (-) ESI-MS analysis of Se-BA-ET and Se-EN-ET solutions:

Ions observed and identified in (-) ESI-MS high-resolution mass spectra of Se-BA-ET and Se-EN-ET solutions are summarized in Table 1. The m/z values listed correspond to the monoisotopic mass for each ion. Elemental compositions and the associated error with respect to the observed m/z vales are also given for each ion. For some ions, the high resolution MS signal was too low for accurate calculation of the error or calculation of the m/z with high accuracy (more than two decimal points). Assignments for these ions were based on low-resolution mass spectra and isotopic distributions. These ions are marked with \*.

Se in BA-ET		
m/z	Elemental Composition	Error from expected mass (+/- ppm)
112.89743	HSSe	13.83
148.02660	$C_5H_{10}NS_2$	11.03
160.84253	$HSe_2$	13.71
227.94314	$C_5H_{10}NS_2Se$	10.41
240.75861	HSe <sub>3</sub>	7.34
320.67581	HSe <sub>4</sub>	7.63
400.59277	HSe <sub>5</sub>	5.68
474.00*	HSe <sub>6</sub>	Signal too low, assigned based on isotopic patterns
550.50*	HSe <sub>7</sub>	Signal too low, assigned based on isotopic patters

Table S2: Elemental composition of ions detected using (-) ESI-MS for Se solutions in BA-ET and EN-ET

Se in EN-ET		
m/z	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
80.92523	HSe	17.69
92.98412	$C_2H_5S_2$	15.08
111.88941	SSe	12.21
140.92852	C <sub>2</sub> H <sub>5</sub> SSe	9.58
160.84194	$HSe_2$	10.07

### **Effect of Thiol Quantity on Selenium Dissolutions:**

#### Raman analysis of Se-BA-ET solutions at different concnetrations:

Figure S5a compiles the Raman spectra for samples with fixed thiol:Se ratio (ET:Se=0.3) at different Se concentrations. These spectra suggest that with amine dilution, the relative ratio of amine peak intensity to Se-Se peak intensity increases. However, all samples show two identical peaks corresponding to polyselenides (linear and possibly cyclic) suggesting no significant effect of Se concentration on the species formed in the solution with amine dilution within 0.01 M - 1.25 M concentration range and fixed thiol:Se ratio. Similarly, Figure S5b compiles the Raman spectra for samples with fixed amine: thiol ratio (BA:ET=5) at different Se concentrations. These solutions yield thiol:Se ratio of 1.5, 12 and 120 for 1.25 M, 0.1 M and 0.01 M samples respectively. As can be seen from the Raman spectra below, this dilution with amine-thiol solution results in drastic increase in intensity for amine and thiol peaks making the relative intensity of Se-Se peak smaller. When analyzed closely, these spectra show presence of a peak at around 246 cm<sup>-1</sup>. Although the peak positions look similar, the peak for higher concentration samples appear skewed with small shoulder on the lower frequency side while the peak for 0.01 M sample looks symmetric. Such non skewed peak for 0.01 M sample could be a result of either steeply decreasing baseline in this sample at lower frequencies hiding this shoulder (mostly arising from strong solvent scattering) or reduced distribution of polyselenides in the solution. While other experiments might be needed to deconvolute this observation, it is important to note that even with extreme dilution using amine-thiol solution (0.01 M Se concentration and thiol:Se ratio of 120) the Se species remain in the form of polyselenides.



Figure S5: Raman spectra of Se-BA-ET solution collected at different concentrations by keeping (a) ET:Se fixed at 0.3 and (b) BA:ET fixed at 5



Figure S6: (a) Se K-edge XANES spectra, (b) the magnitude component and (c.d) the imaginary component of the Fourier transforms (FTs) of Se K-edge k2-weighted EXAFS spectra measured for Se in BA-ET and Se in EN-ET solutions with minimum ET used for dissolution

#### NMR analysis of Se-BA-ET solutions with different thiol quantities:

<sup>1</sup>H-NMR spectra were collected on a Brucker AV-III-400-HD instrument at 400 MHz frequency using CD<sub>3</sub>CN solvent. Ethylene carbonate was used as NMR standard for quantitative analysis. Additional ET in Se-BA solution leads to the formation of diethyldisulfide and its quantity was calculated by integrating the quartet peak at  $\delta$  of 2.72 ppm.



Figure S7: <sup>1</sup>H-NMR speactra of Se-BA-ET solutions with different quantity of thiol used for dissolution. Quartet at  $\delta$  of 2.72 ppm corresponding to diethyldisulfide was used for quantitative measurement with reference to the peak at  $\delta$  of 4.45 ppm corresponding the ethylene carbonate as NMR standard.

#### (-) ESI-MS analysis of Se-BA-ET and Se-EN-ET solutions with minimum ET:

(-) ESI-MS spectra of Se-BA-ET and Se-EN-ET solutions containing minimum ET quantity are shown in Figure S8. Ions observed and identified in these spectra along with their proposed chemical composition are summarized in Table 2. The m/z listed corresponds to the monoisotopic mass for the ion.



Figure S8: (-) ESI-MS spectra of Se-BA-ET solution and Se-EN-ET solution with minimum thiol used for dissolution

For some ions, the high resolution MS signal was too low for accurate calculation of the error or calculation of the m/z with high accuracy (more than two decimal points). Assignments for these ions were based on low-resolution mass and isotopic distributions. These ions are marked in the table with \*.

Se in BA-ET with minimum ET		
m/z	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
105.92037	CNSe	11.73
116.07191	$C_5H_{10}NO_2$	11.24
140.92850	C <sub>2</sub> H <sub>5</sub> SSe	9.59
159.83391	$Se_2$	8.98
220.84506	$C_2H_5SSe_2$	6.20
240.75812	HSe <sub>3</sub>	6.69
300.76171	$C_2H_5SSe_3$	5.14
320.67536	HSe <sub>4</sub>	5.66
400.59350	HSe <sub>5</sub>	8.35
480.58*	HSe <sub>6</sub>	Signal too low

Table S3: Elemental composition of ions detected using (-) ESI-MS for Se solutions in BA-ET and EN-ETwith minimum thiol used for dissolution

Se in EN-ET with minimum ET		
m/z.	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
85.047079	C <sub>3</sub> H <sub>5</sub> ON <sub>2</sub>	13.53
108.99644	$C_2H_5O_3S$	9.62
140.92818	C <sub>2</sub> H <sub>5</sub> SSe	7.17
160.84161	HSe <sub>2</sub>	8.02
220.84452	$C_2H_5SSe_2$	3.75
240.75800	HSe <sub>3</sub>	4.81
300.76146	$C_2H_5SSe_3$	4.15
319.66712	Se <sub>4</sub> /HSe <sub>4</sub>	4.95
400.59241	HSe <sub>5</sub>	6.30
480.58*	HSe <sub>6</sub>	Signal too low

#### NMR analysis of Se-EN-ET solutions with different thiol quantities:

<sup>1</sup>H-NMR spectra were collected on a Brucker AV-III-400-HD instrument at 400 MHz frequency using CD<sub>3</sub>CN solvent. Ethylene carbonate was used as NMR standard for quantitative analysis. Additional ET in Se-BA solution leads to the formation of diethyldisulfide and its quantity was calculated by integrating the quartet peak at  $\delta$  of 2.72 ppm.



Figure S9: <sup>1</sup>H-NMR speactra of Se-EN-ET solutions with different quantity of thiol used for dissolution. Quartet at  $\delta$  of 2.72 ppm corresponding to diethyldisulfide was used for quantitative measurement with reference to the peak at  $\delta$  of 4.45 ppm corresponding the ethylene carbonate as NMR standard.

### **Tellurium Dissolution in Diamine Solutions:**

X-ray Absorption Spectroscopy of Te-EN-ET solution:

Figure S10 summarizes XAS analysis of Te in EN-ET solution.



Figure S10: (a) Te K-edge XANES spectra, (b) the imaginary component of the Fourier transforms (FTs) of Te K-edge k2-weighted EXAFS spectra measured for Te in EN-ET solution

#### (-) ESI-MS analysis of Te-EN-ET solution:

Ions observed and identified in (-) ESI-MS spectra of Te-EN-ET solution are summarized in Table 3. The m/z listed corresponds to the monoisotopic mass for each ion. Elemental compositions and the corresponding error with respect to the observed m/z are also calculated for each ion. For some ions, the high resolution MS signal was too low for accurate calculation of the error or calculation of the m/z with high accuracy (more than two decimal points). Assignments for these ions were based on low-resolution mass and isotopic distributions. These ions are marked in the table with \*.

Te in EN-ET		
m/z,	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
136.95613	$C_3H_5S_3$	9.79
161.87906	STe	8.12
190.91805	C <sub>2</sub> H <sub>5</sub> STe	6.19
260.82089	$HTe_2$	4.48
320.82420	$C_2H_5STe_2$	3.45
389.71815	Te <sub>3</sub> /HTe <sub>3</sub>	0.08
450.75*	$C_2H_5STe_3$	Signal too low
520.67*	HTe <sub>4</sub>	Signal too low

Table S4: Elemental composition of ions detected using (-) ESI-MS for Te solutions in EN-ET

### **Co-dissolution of Tellurium and Selenium:**

#### X-ray Absorption Spectroscopy of Se-Te-BA-ET and Se-Te-EN-ET solutions:

Figure S11 summarizes XAS analysis of Se-Te co-dissolution in BA-ET and EN-ET solutions. The XANES spectra for these two solutions look very similar but the EXAFS analysis of the collected data suggests some difference between neighboring environments of the Se in these two solutions.



Figure S11: (a) The magnitude component and (c,d) the imaginary component of the Fourier transforms (FTs) of Se K-edge k2-weighted EXAFS spectra of Se-Te-BA-ET and Se-Te-EN-ET solutions.

#### (-) ESI-MS analysis of Se-Te-BA-ET and Se-Te-EN-ET solutions:

Ions observed and identified in (-) ESI-MS spectra of Se-Te-BA-ET and Se-Te-EN-ET solutions are summarized in Table 4. The m/z listed corresponds to the monoisotopic mass for each ion. Elemental compositions and the associated error with respect to observed m/z are also calculated for each ion. For some ions, the high resolution MS signal was too low for accurate calculation of the error or calculation of the m/z with high accuracy (more than two decimal points). Assignments for these ions were based on low-resolution mass and isotopic distributions. These ions are marked in the table with \*.

Table S5: Elemental composition of ions detected using (-) ESI-MS for Se-Te solutions in BA-ET	and EN-
ET	

Se-Te in BA-ET		
m/z	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
105.92036	CNSe	12.39
148.02625	$C_5H_{10}NS_2$	9.00
160.84213	HSe <sub>2</sub>	11.25
210.83132	HSeTe	6.16
227.94271	$C_5H_{10}NS_2Se$	5.58
289.73993	Se <sub>2</sub> Te	4.18
370.66490	HSe <sub>3</sub> Te	4.95
420.83*	HSe <sub>2</sub> Te <sub>2</sub>	Signal too low
500.67*	HSe <sub>3</sub> Te <sub>2</sub>	Signal too low

Se-Te in EN-ET		
m/z	<b>Elemental Composition</b>	Error from expected mass (+/- ppm)
105.91988	CNSe	7.86
140.92789	C <sub>2</sub> H <sub>5</sub> SSe	5.11
155.90941	CNTe	4.24
160.84100	HSe <sub>2</sub>	4.23
190.91736	C <sub>2</sub> H <sub>5</sub> STe	2.56
212.84688	H <sub>3</sub> SeTe	5.68
259.81210	$Te_2$	0.78
270.83359	C <sub>2</sub> H <sub>5</sub> SSeTe	0.73
289.73917	Se <sub>2</sub> Te	1.56
320.82318	$C_2H_5STe_2$	0.27
340.83*	HSeTe <sub>2</sub>	Signal too low
370.75*	HSe <sub>3</sub> Te	Signal too low
420.83*	HSe <sub>2</sub> Te <sub>2</sub>	Signal too low

# **Tuning Material Synthesis through Discovered Chemical Understanding:**

<u>SEM analysis of  $PbSe_nTe_{1-n}$  particles synthesized from Se-Te-BA-ET and Se-Te-EN-ET solutions:</u>



*Figure S12: SEM images of the PbSe<sub>n</sub>Te<sub>1-n</sub> particles synthesized using (a) Se-Te-BA-ET solution and (b) Se-Te-EN-ET solution*