






# Catenated and Spirocyclic Polychalcogenides from Potassium Carbonate and Elemental Chalcogens

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## Supplementary Information

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## 1. Experimental section

**General procedures:** The preparations were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. All starting materials were obtained from commercial sources (Sigma-Aldrich) and used as received. The NMR spectra were recorded in DMSO- $d_6$  solutions on a Bruker-AVANCE-DMX400 ( $^1\text{H}$ : 400.1 MHz;  $^{13}\text{C}$ : 100.6 MHz).  $^1\text{H}$  and  $^{13}\text{C}$  shifts are referenced to internal solvent resonances and reported in parts per million (ppm) relative to tetramethylsilane. IR spectra were measured using Bruker-Optics VERTEX 70v spectrometer equipped with a diamond ATR unit between  $4000\text{ cm}^{-1}$  and  $50\text{ cm}^{-1}$ . Microanalyses of the compounds were performed using a "VARIO EL cube" apparatus from Elementar Analysensysteme GmbH. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed simultaneously using a Netsch STA 449. The samples were measured in the range from  $30\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$  with a  $5\text{K/min}$  heating rate under nitrogen.

### Preparation of $(\text{PPN})_2\text{S}_{12}$ (**1**)

The dodecasulfide salt **1** was prepared using a slight modification of the original procedure published by Seel and Wagner.<sup>S1</sup> In a 200 ml Schlenk tube, finely powdered anhydrous potassium carbonate (2.0 g, 14.5 mmol),  $\text{S}_8$  (2.0 g, 7.8 mmol) and  $(\text{PPN})\text{Cl}$  (1.0 g, 1.74 mmol) were mixed and suspended in 10 ml of dry acetone. The mixture was stirred for 2 h at r.t. and allowed to stand undisturbed at r.t. for 3–4 d. During this time, the resulting orange-red suspension became interspersed with well-formed black-purple crystals of **1**, while the supernatant solution turned dark red. The following work-up was carried out in air. The majority of fine particles were decanted after swirling, the residue was re-suspended in 10 ml of acetone and isolated by filtration. The solid was stirred two times for ca. 5 min with 100 ml water in order to remove unreacted potassium carbonate and  $(\text{PPN})\text{Cl}$ . After filtration and drying of the residue *in vacuo*, the crude product was freed from unreacted  $\text{S}_8$  by extraction with  $5 \times 50\text{ ml}$  of toluene. Repeated preparations gave an average isolated yield of ca. 0.5 g (39% based on  $(\text{PPN})\text{Cl}$ ). M.p.  $188\text{ }^\circ\text{C}$  (dec.). Elemental analysis calculated for  $\text{C}_{72}\text{H}_{60}\text{N}_2\text{P}_4\text{S}_{12}$  ( $M = 1461.97\text{ g/mol}$ ): C 59.15, H 4.14, N 1.92, S 26.32; found: C 58.69, H 4.10, N 1.90, S 27.52%. IR (ATR):  $\nu_{\text{max}}$  3052 w, 1676 m, 1586 w, 1481 w, 1436 m, 1407 w, 1261 s, 1182 m, 1161 w, 1112 s, 1054 m, 1024 m, 996 m, 977 m, 935 w, 918

m, 852 w, 798 w, 745 m, 722 vs, 690 vs, 617 w, 603 w, 547 s, 531 vs, 495 vs, 439 m, 394 m, 351 w, 325 m, 239 w, 200 m, 91 m, 70 m, 61 m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (27 °C, DMSO- $d_6$ , 400 MHz):  $\delta$  7.73 – 7.68 (m, 12H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.63 – 7.52 (m, 48 H, *o/m*-C<sub>6</sub>H<sub>5</sub>) ppm.  $^{13}\text{C}$  NMR (27 °C, DMSO- $d_6$ , 100 MHz):  $\delta$  133.5 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 131.8 (m, *o*-C<sub>6</sub>H<sub>5</sub>), 129.4 (m, *m*-C<sub>6</sub>H<sub>5</sub>), 126.6 (dd, *ipso*-C<sub>6</sub>H<sub>5</sub>, d,  $^1J_{\text{C,P}} = 107$  Hz,  $^3J_{\text{C,P}} = 2$  Hz) ppm.  $^{31}\text{P}$  NMR (27 °C, DMSO- $d_6$ , 162 MHz):  $\delta$  20.6 ppm.

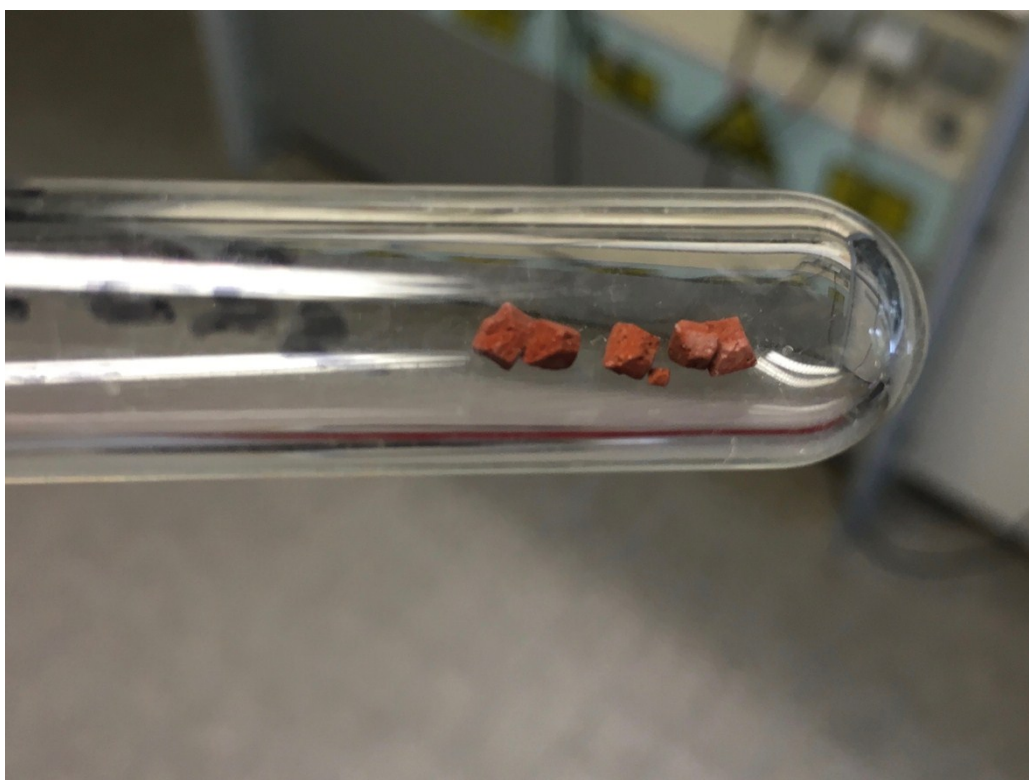
### Preparation of (PPN)<sub>2</sub>Se<sub>11</sub> (**2**)

The undecaselenide salt **2** was prepared in a similar manner as described for **1** using 4.0 g of powdered grey selenium instead of elemental sulfur. The reaction mixture was stirred at reflux temperature for 5 h. After cooling to r.t., all insoluble material was removed by filtration and the deep green filtrate was concentrated to a total volume of ca. 5 ml. Crystallization at r.t. for 2 d yielded 0.24 g (14% based on (PPN)Cl) of **2** as greenish-black, moderately air-sensitive crystals. Although being rather low, the isolated yield could be reproducibly obtained in several preparations. M.p. 156 °C. Elemental analysis calculated for C<sub>72</sub>H<sub>60</sub>N<sub>2</sub>P<sub>4</sub>Se<sub>11</sub> (M = 1945.74 g/mol): C 44.45, H 3.11, N 1.44; found: C 44.60, H 3.16, N 1.42%. IR (ATR):  $\nu_{\text{max}}$  3047 w, 3006 w, 2327 w, 2086 w, 1996 w, 1893 w, 1815 w, 1586 m, 1572 w, 1480 m, 1435 s, 1287 s, 1269 m, 1183 m, 1158 w, 1116 s, 1070 w, 1026 w, 995 m, 972 w, 923 w, 848 m, 792 w, 743 m, 723 vs, 688 vs, 615 m, 546 s, 523 vs, 498 vs, 450 m, 385 m, 352 w, 316 m, 272 w, 251 w, 225 w, 198 w, 183 w, 137 m, 113 s, 95 s, 55 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (27 °C, DMSO- $d_6$ , 400 MHz):  $\delta$  7.74 – 7.69 (m, 12H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.63 – 7.53 (m, 48 H, *o/m*-C<sub>6</sub>H<sub>5</sub>) ppm.  $^{13}\text{C}$  NMR (27 °C, DMSO- $d_6$ , 100 MHz):  $\delta$  134.2 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 132.5 (m, *o*-C<sub>6</sub>H<sub>5</sub>), 130.0 (m, *m*-C<sub>6</sub>H<sub>5</sub>), 127.1 (dd, *ipso*-C<sub>6</sub>H<sub>5</sub>, d,  $^1J_{\text{C,P}} = 106$  Hz,  $^3J_{\text{C,P}} = 2$  Hz) ppm.  $^{31}\text{P}$  NMR (27 °C, DMSO- $d_6$ , 162 MHz):  $\delta$  21.3 ppm.

## 2. Crystal photos of compounds **1** and **2**



**Fig. S1.** As-prepared sample of  $(\text{PPN})_2\text{S}_{12}$  (**1**).

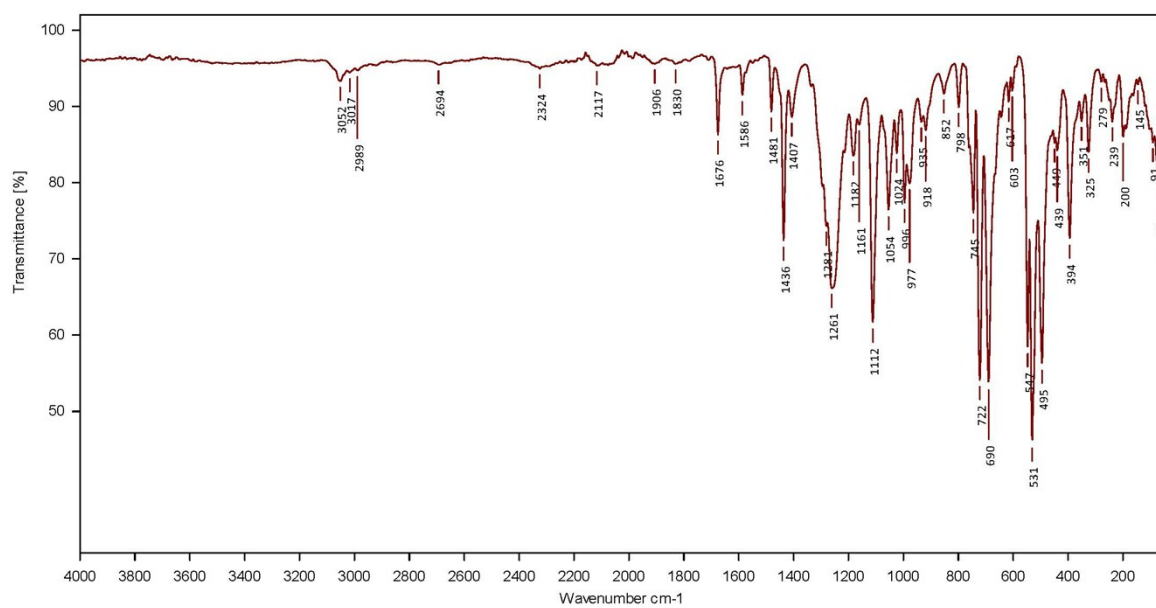


**Fig. S2.** Crystals of **1** after washing with  $\text{CS}_2$ .

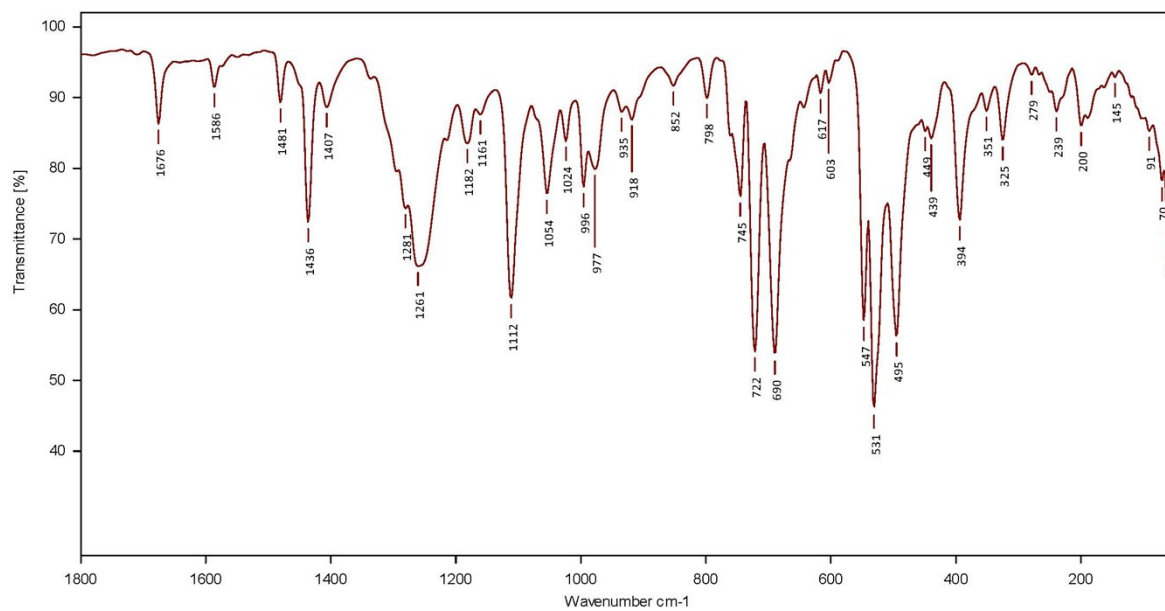


**Fig. S3.** Crystals of **2** with 20x magnification.

### 3. IR spectra of compounds **1** and **2**



**Fig. S4.** Full IR spectrum of **1**.



**Fig. S5.** Fingerprint region of the IR spectrum of **1**.



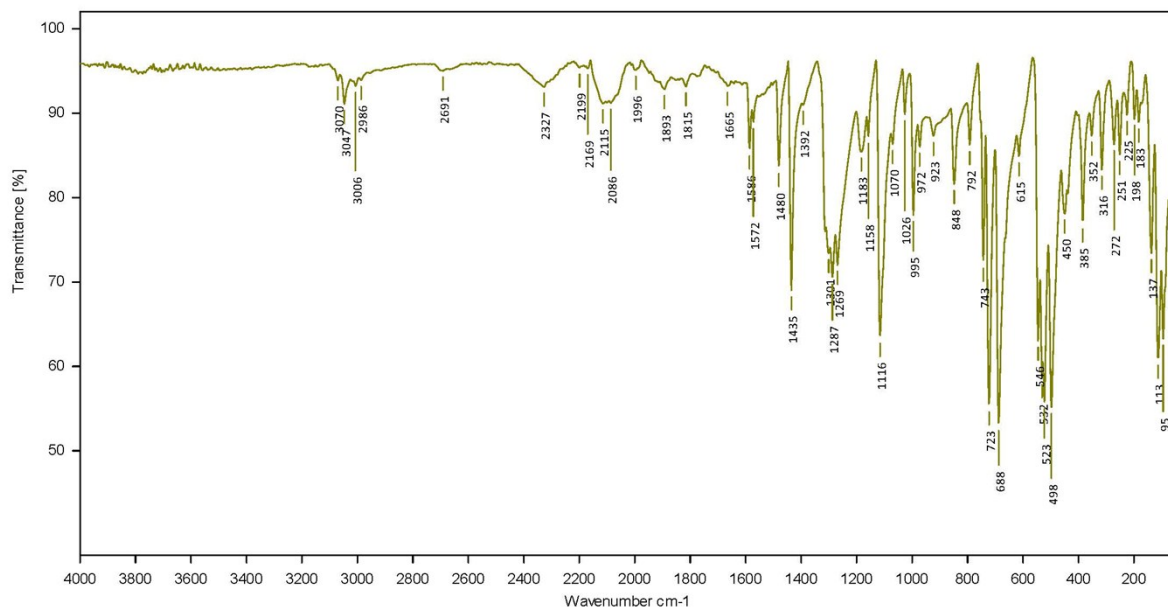


Fig. S6. Full IR spectrum of 2.

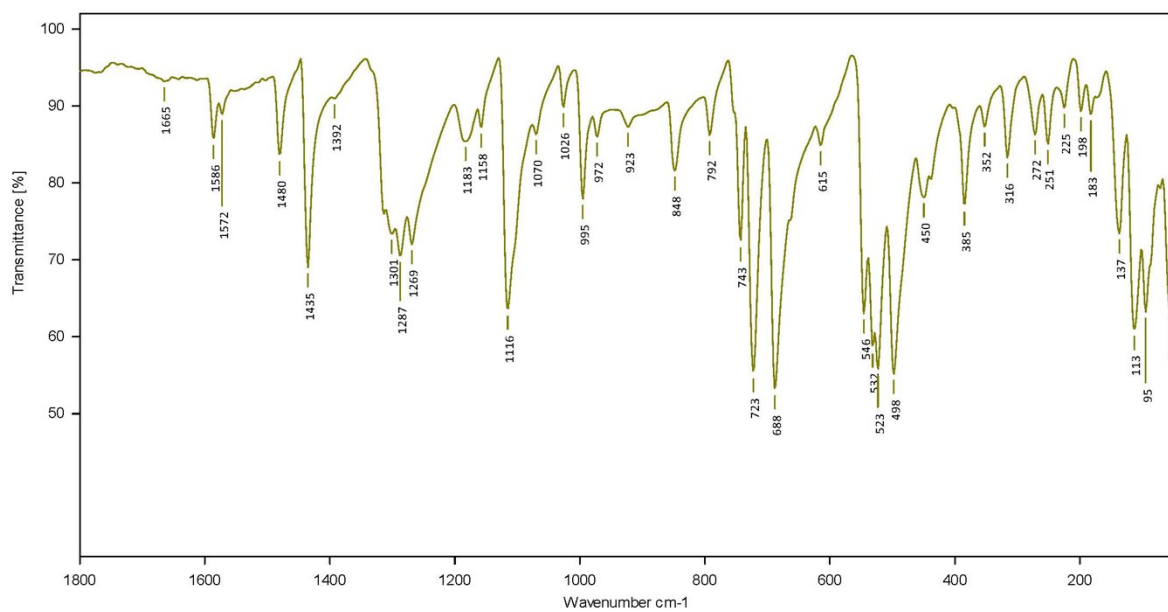
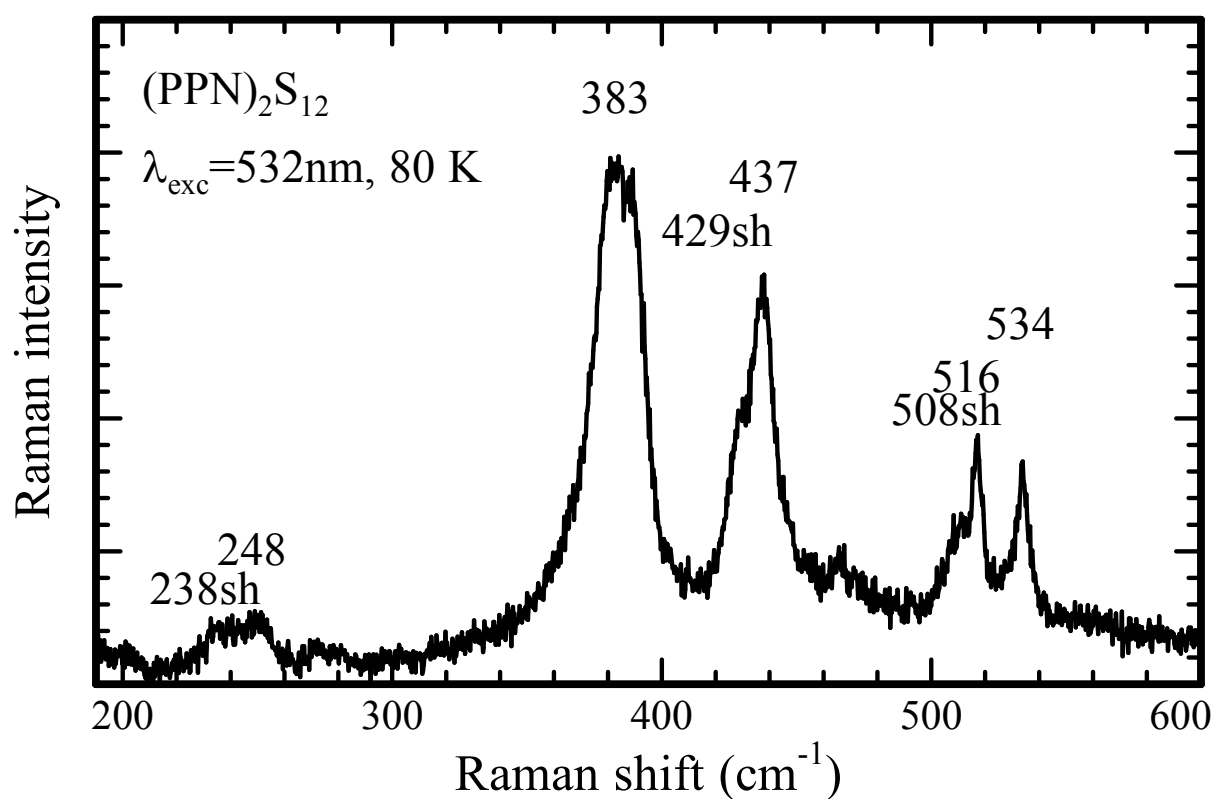


Fig. S7. Fingerprint region of the IR spectrum of 2.



#### 4. Raman spectra of compounds **1** and **2**

Raman spectroscopy was performed using a Raman microscope (TriVista777, S&I, Germany) in single monochromator mode. As excitation, a 532 nm frequency doubled YAG:Nd laser was selected. The excitation intensity was chosen carefully to avoid damage to the samples under study. The sample crystals were placed in a vacuumized cryostat cooled by liquid nitrogen to allow for low-temperature spectra. The spectra shown here (Figs. S8 and S9) were recorded at  $T = 80$  K. The Raman signals of the scattered light were separated by a Bragg filter, i.e. only the Stokes side of the spectra is investigated here.



**Fig. S8.** Raman spectrum of **1**.

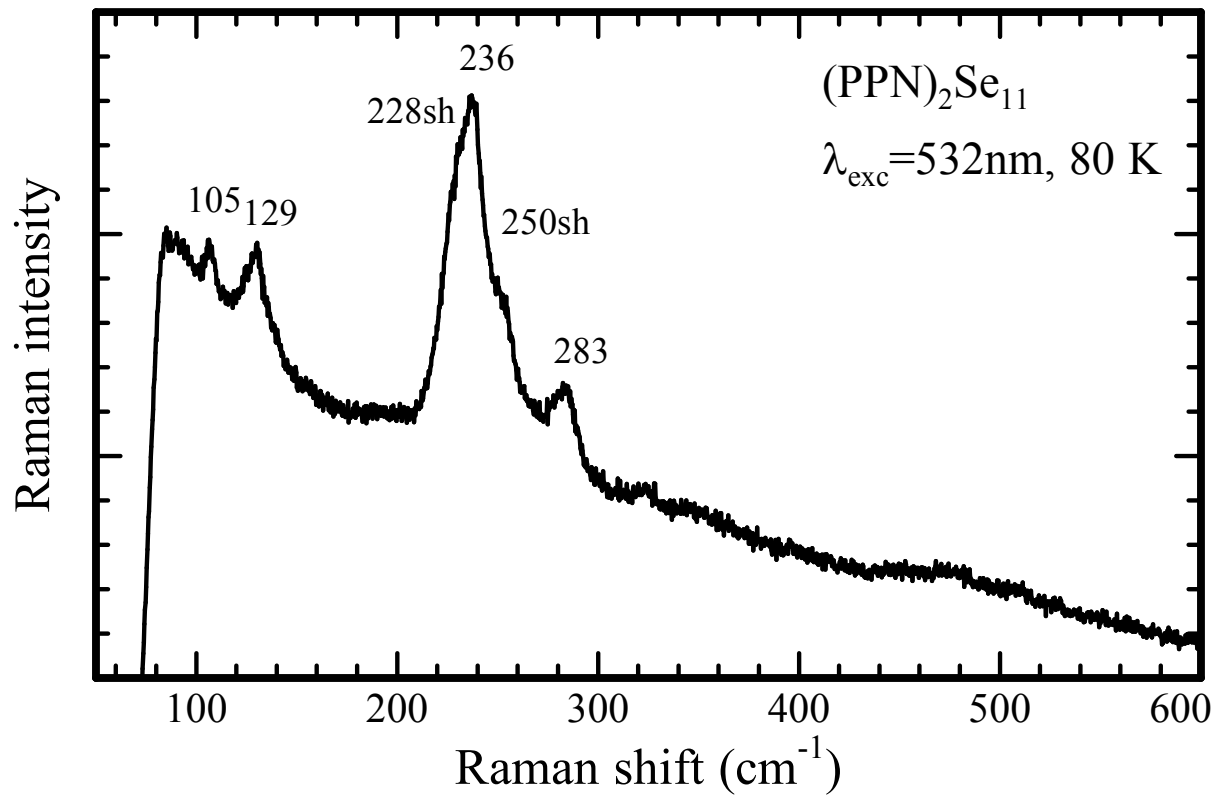
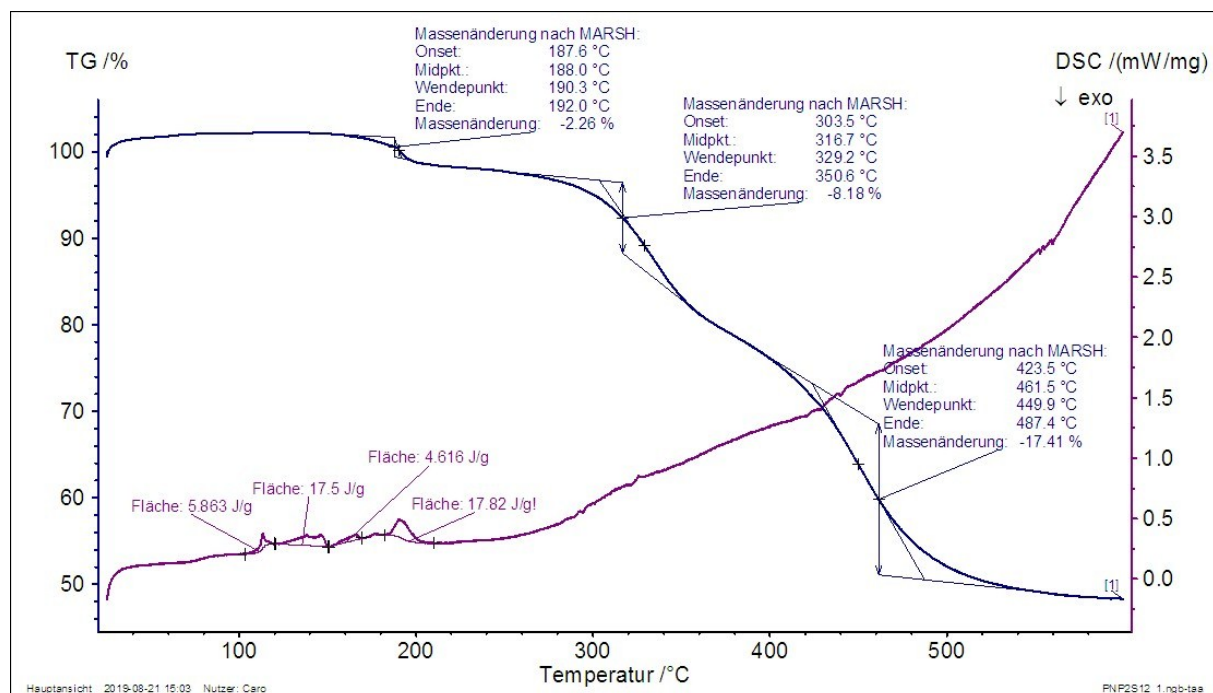
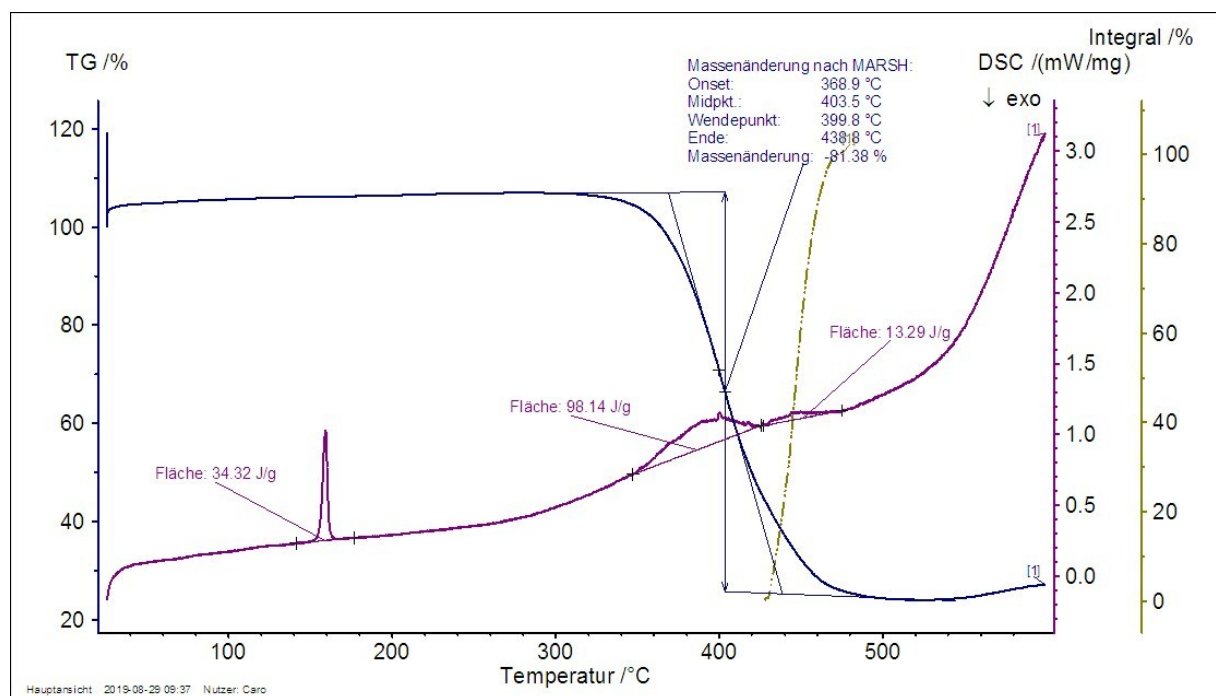


Fig. S9. Raman spectrum of 2.

5. TG-DSC diagrams of compounds **1** and **2**

**Fig. S10.** Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) for compound **1** under nitrogen.



**Fig. S11.** Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) for compound **2** under nitrogen.

## 6. X-Ray crystallographic data of compounds **1** and **2**

Single crystal X-ray intensity data of **1** and **2** were collected on a STOE IPDS 2T diffractometer equipped with a 34 cm image plate detector at  $T = 153(2)$  K, using graphite-monochromated Mo- $K_{\alpha}$  radiation. Numerical absorption correction was applied on the intensity data.<sup>S2</sup> The structures were solved with SHELXT-2015<sup>S3</sup> and refined by full matrix least-squares methods on  $F^2$  using SHELXL-2016.<sup>S4</sup>

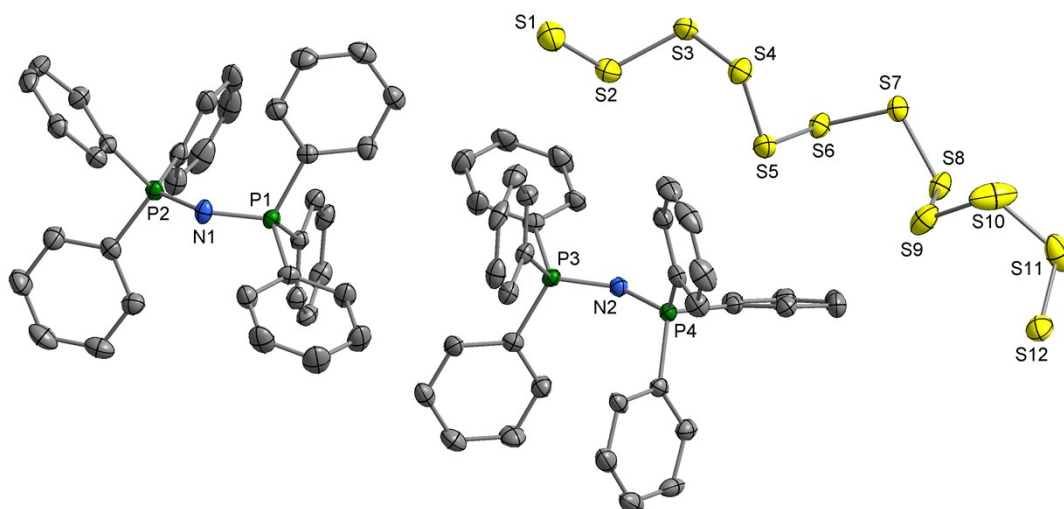
Crystallographic data for the structure reported in this paper have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers 1959714 (**1**) and 1959715 (**2**) (Fax: +44-1223-336-033; E-Mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk), <http://www.ccdc.cam.ac.uk>).

**Table S1.** Crystal data and details on structure refinement for compounds **1** and **2**.

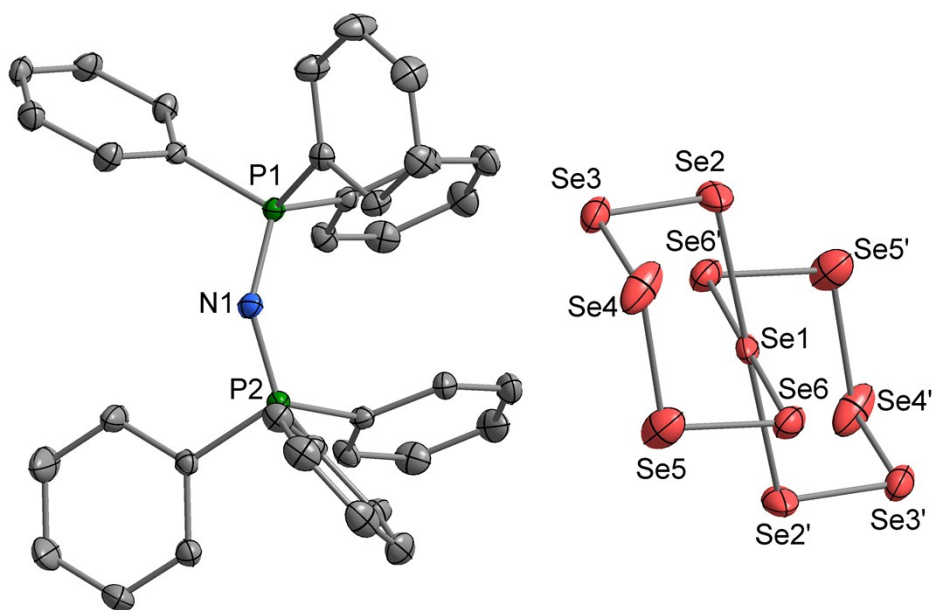
Compound	<b>1</b>	<b>2</b>
CCDC deposition number	1959714	1959715
Molecular formula	C <sub>72</sub> H <sub>60</sub> N <sub>2</sub> P <sub>4</sub> S <sub>12</sub>	C <sub>72</sub> H <sub>60</sub> N <sub>2</sub> P <sub>4</sub> Se <sub>11</sub>
Formula weight / g mol <sup>-1</sup>	1461.82	1945.66
Crystal system	monoclinic	monoclinic
Space group	Cc	P2 <sub>1</sub> /c
Cell metric		
<i>a</i> / Å	13.6600(3)	10.9704(3)
<i>b</i> / Å	14.2151(3)	18.3061(4)
<i>c</i> / Å	35.8526(9)	17.7630(5)
α / deg.	90	90
β / deg.	95.642(2)	95.713(2)
γ / deg.	90	90
Cell volume / Å <sup>3</sup>	6928.1(3)	3549.5(2)
Molecules per cell <i>z</i>	4	2
Electrons per cell <i>F</i> <sub>000</sub>	3032	1880
Calcd. density ρ / g cm <sup>-3</sup>	1.401	1.820
μ / mm <sup>-1</sup> (Mo-Kα)	0.516	5.790
Crystal shape and color	dark violet prism	dark green prism
Crystal size / mm	0.37×0.31×0.17	0.39×0.25×0.23
θ range / deg.	2.073 ... 25.104	2.172 ... 29.240
Reflections collected	16543	26598
Reflections unique	9530	9545
Reflections with <i>I</i> >2σ( <i>I</i> )	9065	7086
Completeness of dataset	96.2%	99.7%
<i>R</i> <sub>int</sub>	0.0219	0.0504
Parameters; Restraints	812; 2	403; 0
<i>R</i> <sub>1</sub> (all data, <i>I</i> >2σ( <i>I</i> ))	0.0385; 0.0351	0.0732; 0.0439
<i>wR</i> <sub>2</sub> (all data, <i>I</i> >2σ( <i>I</i> ))	0.0879; 0.0852	0.0872; 0.0776
GooF ( <i>F</i> <sup>2</sup> )	1.054	1.116
Max. residual peaks	-0.642; 0.732	-0.914; 0.945
Flack parameter	0.34(7) <sup>a</sup>	-

<sup>a</sup> refined as an inversion twin.

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**Figure S12.** Molecular structure of **1** in the crystalline state. Displacement ellipsoids drawn at the 50% probability level, H atoms omitted for clarity.



**Figure S13.** Molecular structure of **2** in the crystalline state. Displacement ellipsoids drawn at the 50% probability level, H atoms omitted for clarity.



## 7. References

- S1 F. Seel and M. Wagner, *Z. Naturforsch.*, 1985, **40B**, 762-764
- S2 Stoe & Cie 2002, *X-Area and X-Red*, Stoe & Cie, Darmstadt, Germany.
- S3 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
- S4 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.